

Proc. NATO Advanced Study  
Institute on Semiclassical  
Methods in Scattering and  
Spectroscopy (1979)

(NASA-CR-158776) SEMICLASSICAL THEORY OF  
ELECTRONICALLY NONADIABATIC TRANSITIONS IN  
MOLECULAR COLLISION PROCESSES (Rochester  
Univ.) 83 p HC A05/MF A01

N79-27944

CSSL 07D

Unclass

G3/72 27869

SEMICLASSICAL THEORY OF ELECTRONICALLY NONADIABATIC TRANSITIONS  
IN MOLECULAR COLLISION PROCESSES\*

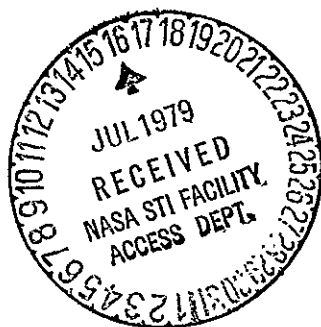
Kai S. Lam and Thomas F. George<sup>†</sup>

Department of Chemistry  
University of Rochester  
Rochester, New York, U.S.A.

An introductory account of the semiclassical theory of the S-matrix for molecular collision processes is presented, with special emphasis on electronically nonadiabatic transitions. This theory is based on the incorporation of classical mechanics with quantum superposition, and in practice makes use of the analytic continuation of classical mechanics into the complex space or time domain. After a brief discussion of the relevant concepts of molecular scattering theory and related dynamical models, the formalism is developed and illustrated with simple examples - collinear collision of the A+BC type. The theory is then extended to include the effects of laser-induced nonadiabatic transitions. The lecture concludes with a discussion of two bound continuum processes - collisional ionization and collision-induced emission - also amenable to the same general semiclassical treatment.

\* Project supported by the U.S. Air Force Office of Scientific Research (Contract No. F49620-78-C-0005), the National Science Foundation (Grant No. CHE77-27826) and the National Aeronautics and Space Administration (Grant No. NSG-2198).

<sup>†</sup> Camille and Henry Dreyfus Teacher-Scholar (1975-80) and Alfred P. Sloan Research Fellow (1976-80).



## I. INTRODUCTORY CONCEPTS AND TOOLS

### 1a. Scattering Matrices and Scattering Cross-Sections

In scattering experiments of any kind, the fundamental observable quantity is the scattering cross section; and the theoretical object of prime importance associated with it is the scattering matrix (or S-matrix). We begin by giving formal definitions of the S-matrix applicable to general scattering processes and in later sections adapt them to molecular collision problems. The S-matrix will be shown to be directly related to the scattering cross section through an auxiliary object, the transition matrix (or T-matrix); and a key objective of the theoretical program of collision processes is the calculation of S- or T-matrices.

S- and T-matrices are quantum mechanical objects and they will be introduced as such in the present subsection. However, under certain conditions, such as in the treatment of heavy-particle dynamics in molecular collisions they can be adapted to semiclassical or even classical evaluations. In the present lecture series we shall focus on the semiclassical evaluation of the S-matrix (called the "semiclassical S-matrix"), with special applications to the case of electronically non-adiabatic transitions. Before discussing this explicitly, we shall review some basic ideas associated with the S-matrix in general.

A collision system can be thought of as being in the states  $\psi^{\text{in}}$  (incoming) and  $\psi^{\text{out}}$  (outgoing) before and after the collision process respectively; and the collision can be visualized as a "blackbox" mathematically described by a transformer operator S (the scattering operator) such that

$$\psi^{\text{out}} = S\psi^{\text{in}} . \quad (\text{Ia.1})$$

Suppose  $\psi^{\text{in}}$  is specified by a given free state  $|i\rangle$  (this state is often chosen to be an eigenstate of the unperturbed Hamiltonian).  $\psi^{\text{out}}$  can be expanded in terms of the complete set of which  $|i\rangle$  is a member

$$\psi^{\text{out}} = \sum_j c_j |j\rangle . \quad (\text{Ia.2})$$

The transition probability amplitude from  $|i\rangle$  to a particular  $|f\rangle$  is then given by

$$c_f = \langle f | \psi^{\text{out}} \rangle = \langle f | S | \psi^{\text{in}} \rangle = \langle f | S | i \rangle \equiv S_{fi} . \quad (\text{Ia.3})$$

Hence, it is seen that  $S_{fi}$ , which is a matrix element of the scattering operator  $S$  in the  $|i\rangle$  representation, gives directly the transition probability amplitude from the state  $|i\rangle$  to the state  $|f\rangle$ . We note that the conservation of probability for  $\psi^{in}$  and  $\psi^{out}$  requires that

$$\langle \psi^{out} | \psi^{out} \rangle = \langle \psi^{in} | \psi^{in} \rangle , \quad (Ia.4)$$

implying that

$$S^\dagger S = S S^\dagger = 1 , \quad (Ia.5)$$

which is a statement of the unitarity of the  $S$ -matrix.

The definition of  $S$  can also be formulated in the time-dependent formalism, if we set

$$\begin{aligned} \psi^{in} &= \psi(t=-\infty) \\ \psi^{out} &= \psi(t=+\infty) . \end{aligned} \quad (Ia.6)$$

Then  $S$  can be defined by

$$\Psi(+\infty) = S\Psi(-\infty) , \quad (Ia.7)$$

and is also expressible as

$$S = \lim_{\substack{t \rightarrow +\infty \\ t_0 \rightarrow -\infty}} U(t, t_0) , \quad (Ia.8)$$

where  $U$  is the time evolution-operator for the interaction picture wave function.

In order to calculate the scattering cross section from the  $S$ -matrix, we first evaluate the transition probability per unit time  $W_{i \rightarrow f}$ , since the cross section  $\sigma_{i \rightarrow f}$  is defined as

$$\sigma_{i \rightarrow f} = \frac{W_{i \rightarrow f}}{F_i} , \quad (Ia.9)$$

where  $F_i$  is the incident flux of particles for the state  $|i\rangle$ . Now  $S$ , as defined earlier, is the transition probability amplitude between infinite past and infinite future times. To find the probability per unit time, we must express it as the limit of a time-dependent quantity  $\tilde{S}_{fi}(t)$  for  $i \neq f$  (transition between different states) such that

$$S_{fi} = \lim_{t \rightarrow +\infty} \tilde{S}_{fi}(t) . \quad (Ia.10)$$

The transition probability per unit time  $W_{i \rightarrow f}$  can then be defined as

$$W_{i \rightarrow f} = \lim_{t \rightarrow \infty} \frac{|\tilde{S}_{fi}(t)|^2}{t} . \quad (Ia.11)$$

Since we are interested in transitions between different states  $|i\rangle$  and  $|f\rangle$ , it is reasonable to extract from  $S$  a term which is zero when  $i$  and  $f$  are indeed different, namely  $\delta_{fi}$ . Also, since energy conservation holds between infinite past and future times, we can further separate out an energy conservation factor  $\delta(E_i - E_f)$  in the remainder term. Hence we write

$$S_{fi} \equiv \delta_{fi} - 2\pi i \delta(E_i - E_f) T_{fi} . \quad (Ia.12)$$

The factor  $2\pi i$  is introduced for convenience; and  $T$ , whose matrix elements are  $T_{fi} = \langle f | T | i \rangle$ , is called the transition or T-matrix. Written as in (Ia.12) with an explicit energy dependence,  $S_{fi}$  (for  $i \neq f$ ) can now be expressed as

$$S_{fi} = -2\pi i \delta(E_i - E_f) T_{fi} \equiv \lim_{t \rightarrow \infty} \tilde{S}_{fi}(t) . \quad (Ia.13)$$

This identifies  $\tilde{S}_{fi}(t)$  as

$$\begin{aligned} \tilde{S}_{fi}(t) &= -\frac{i}{\hbar} T_{fi} \int_{-t/2}^{t/2} dt' e^{i(E_i - E_f)t'/\hbar} \\ &= -\frac{i}{\hbar} t T_{fi} \frac{\sin\{(E_i - E_f)t/2\hbar\}}{(E_i - E_f)t/2\hbar} \end{aligned} \quad (Ia.14)$$

which represents a transition probability amplitude for  $i \rightarrow f$  over a finite period  $t$  of observation. The transition probability per unit time, from (Ia.11), is then given by

$$W_{i \rightarrow f} = \frac{|T_{fi}|^2}{\hbar^2} \lim_{t \rightarrow \infty} \frac{\sin^2\{(E_i - E_f)t/2\hbar\}}{\left(\frac{E_i - E_f}{2\hbar}\right)^2 t} \quad (Ia.15)$$

which is equivalent to

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} \delta(E_i - E_f) |T_{fi}|^2 , \quad f \neq i . \quad (Ia.16)$$

In general, in any experimental situation, there will be a group of final states  $|f\rangle$  satisfying energy conservation, and the

scattering cross-section observed will correspond to the sum over these final states. From (Ia.9),

$$\sigma_{i \rightarrow f} = \frac{1}{F_i} \sum_f W_{i \rightarrow f} \quad (\text{Ia.17})$$

The sum will go over to  $\int dE_f \rho(E_f)$  if we are dealing with continuum states in the product channels;  $\rho(E_f)$  is the density of states.

Before leaving our formal discussion of the S-matrix we will point out a formal relation between it and the Green's function to set the stage for the introduction of the semiclassical S-matrix in Section Id.

The operator  $(E-H+i\eta)^{-1}$  ( $\eta$  being infinitesimal) is called the retarded Green's function operator and is directly related to the T-matrix, and hence the S-matrix:

$$G^+(E) = G_0^+(E) + G_0^+(E) T G_0^+(E) \quad (\text{Ia.18})$$

where  $G_0^+(E) = (E-H_0+i\eta)^{-1}$  is the unperturbed retarded Green's function operator. The Fourier transform  $G^+(t)$  of  $G^+(E)$  is given by

$$G^+(t) = \frac{1}{2\pi\hbar} \lim_{\eta \rightarrow 0} \int_{-\infty}^{\infty} dE e^{iEt/\hbar} (E-H+i\eta)^{-1} \quad (\text{Ia.19})$$

By actually evaluating the integral in (Ia.19),  $G^+(E)$  can be written as the inverse Fourier transform of  $G^+(t)$ :

$$G^+(E) = (i/\hbar) \int_0^{\infty} dt \exp(iEt/\hbar) \exp(-iHt/\hbar) \quad (\text{Ia.20})$$

(Ia.18) and (Ia.20) will be the starting point for our formulation of the semiclassical S-matrix in Section Id.

#### 1b. Partitioning of the Molecular Collision Hamiltonian

Beginning with this subsection we will restrict our attention to molecular collision problems, and the general formulation of the S-matrix given earlier will be adapted accordingly. To prepare ourselves for these special formulations of the S-matrix we will start with a discussion of the molecular collision Hamiltonian.

Separation of Electronic and Nuclear Motion and the Born-Oppenheimer Approximation. Consider a molecular collision system with  $n$  electrons and  $N$  nuclei, with electronic coordinates denoted by  $\vec{r}_i$  and nuclear coordinates by  $\vec{R}_i$ . The total Hamiltonian can be written as

$$\begin{aligned}
H &= T_R + T_r + V(\vec{R}, \vec{r}) \\
&\equiv T_R + H_{el}(\vec{R}, \vec{r}) \quad (\text{Ib.1})
\end{aligned}$$

where  $H_{el}(\vec{R}, \vec{r})$  stands for that part of  $H$  besides the nuclear kinetic energy operator. The first-step to simplify the Hamiltonian is to separate out the center of mass motion of the whole system. The dynamics of the system is then described by an arbitrary set of  $(3N+3n-3)$  independent internal coordinates. Several choices of these can be made to suit particular problems, but here we will not be concerned with the specific choices. In general one attempts to make coordinate transformations which would leave the total kinetic energy operator in the form

$$T = -\frac{\hbar^2}{2M} \nabla_S^2 - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{R_i}^2}{\mu_i} - \frac{\hbar^2}{2\mu_e} \sum_i \nabla_{r_i}^2 + (\text{m.p.}) \quad (\text{Ib.2})$$

where (m.p.) represents mass polarization terms (proportional to  $\nabla_{R_i} \cdot \nabla_{R_j}$  and  $\nabla_{r_i} \cdot \nabla_{r_j}$ ) which can be ignored. In (Ib.2),  $M$  stands

for the 'total mass' corresponding to some C.M. coordinate  $\vec{S}$ ;  $\mu_i$  and  $\mu_e$  are the reduced nuclear and electronic masses corresponding to the nuclear internal coordinates  $\vec{R}_i$  and electronic internal coordinates  $\vec{r}_i$  respectively. The total Hamiltonian can be written in terms of the transformed coordinates as

$$\begin{aligned}
H &= -\frac{\hbar^2}{2M} \nabla_S^2 - \frac{\hbar^2}{2} \sum_{i=1}^{N=1} \frac{1}{\mu_i} \nabla_{R_i}^2 - \frac{\hbar^2}{2\mu_e} \sum_{i=1}^n \nabla_{r_i}^2 + V(\vec{R}, \vec{r}) . \\
&\quad (\text{Ib.3})
\end{aligned}$$

$V(\vec{R}, \vec{r})$  may be taken to include spin-orbit interactions. The Hamiltonian in terms of the  $3N+3n-3$  internal coordinates becomes

$$\begin{aligned}
H &= -\frac{\hbar^2}{2} \sum_i \frac{1}{\mu_i} \nabla_{R_i}^2 - \frac{\hbar^2}{2\mu_e} \sum_i \nabla_{r_i}^2 + V(\vec{R}, \vec{r}) \\
&\equiv T_R + H_{el}(\vec{R}, \vec{r}) , \quad (\text{Ib.4})
\end{aligned}$$

where

$$T_R \equiv -\frac{\hbar^2}{2} \sum_i \frac{1}{\mu_i} \nabla_{R_i}^2 .$$

(Ib.4) looks identical to (Ib.1), except now  $\vec{R}$  and  $\vec{r}$  are understood to be the internal coordinates with the C.M. motion separated out. Hamiltonians will be written in this sense for all our later discussions.

Separation of electronic and nuclear motions ultimately

depends on the great disparity between electronic and nuclear masses. Since the forces acting on them are of comparable orders of magnitude, nuclear motions tend to be much more sluggish than electronic motions and electrons can be assumed to adjust to the nuclear motions adiabatically. This consideration is the basis of the Born-Oppenheimer approximation, which in general means the assumption of the existence of some basis set of electronic wave functions  $\phi_k(\vec{r};\vec{R})$  which depend parametrically on the nuclear positions  $\vec{R}$ , and for any fixed  $\vec{R}$  is orthonormal and complete:

$$\int d^3r \phi_k^*(\vec{r};\vec{R}) \phi_\ell(\vec{r};\vec{R}) \equiv \langle \phi_k | \phi_\ell \rangle = \delta_{k\ell} \quad \text{fixed } \vec{R}, \quad (\text{Ib.5})$$

$$1 = \sum_\ell |\phi_\ell\rangle \langle \phi_\ell| \quad \text{fixed } \vec{R}, \quad (\text{Ib.6})$$

such that the total wave function  $\psi(\vec{R},\vec{r})$  of the collision system can be expanded as

$$\psi(\vec{r},\vec{R}) = \sum_\ell \chi_\ell(\vec{R}) \phi_\ell(\vec{r};\vec{R}). \quad (\text{Ib.7})$$

Adiabatic vs Diabatic Representation - Nonadiabatic Couplings and Transitions. The nuclear wave function  $\chi_\ell(\vec{R})$  describes the motion of the nuclei on the potential surface associated with electronic state  $\ell$ . We will see below what we mean by these surfaces when different basis sets  $\phi_\ell$  are chosen. Specifically, we will see how the different choices will lead to the adiabatic and diabatic representations. The function  $\chi_\ell(\vec{R})$  will asymptotically ( $\vec{R} \rightarrow \infty$ ) give the amplitude for the probability that the system ends up in the electronic state  $\phi_\ell$  and thus directly gives the S-matrix for this transition (whose initial state is specified by the problem). Hence, our objective of obtaining the S-matrix reduces, quantum mechanically, to the solution of the Schrödinger equation for  $\chi_\ell(\vec{R})$ .

The time-independent Schrödinger equation to be solved is

$$H\psi(\vec{r},\vec{R}) = E\psi(\vec{r},\vec{R}) \quad (\text{Ib.8})$$

where H is given by (Ib.4). Substitution of (Ib.7) into (Ib.8) results in the coupled set of equations for  $\chi_\ell(\vec{R})$ :

$$(T_R + T_{ii}'' + U_{ii} - E)\chi_i = - \sum_{j \neq i} (T_{ij}' + T_{ij}'' + U_{ij})\chi_j \quad (\text{Ib.9})$$

where

$$U_{ij} = \langle \phi_i | H_{el} | \phi_j \rangle \quad (\text{Ib.10})$$

$$T'_{ij} = \sum_{k=1}^{N-1} \left( \frac{-\hbar^2}{\mu_k} \right) \langle \phi_i | \nabla_{R_k} \phi_j \rangle \cdot \nabla_{R_k} \quad (\text{Ib.11})$$

$$T''_{ij} = \sum_{k=1}^{N-1} \left( \frac{-\hbar^2}{2\mu_k} \right) \langle \phi_i | \nabla_{R_k}^2 \phi_j \rangle . \quad (\text{Ib.12})$$

Brackets denote integration over electronic coordinates  $\vec{r}$  only. The diagonal elements  $U_{ij}(\vec{R})$  are the effective potential energy surfaces mentioned earlier that govern nuclear motion. The diagonal terms  $T''_{ii}(\vec{R})$ , which are nonadiabatic corrections to the potential energy surfaces, are usually small and can be ignored. From (Ib.9) it is seen that motion on the different surfaces are coupled by the off-diagonal elements  $T'_{ij}$ ,  $T''_{ij}$  and  $U_{ij}$ .  $T'_{ij}$  and  $T''_{ij}$  are usually called nonadiabatic couplings, of which  $T'_{ij}$  are the dominant ones (dependent only on the first derivative of  $\phi$  with respect to nuclear coordinates) and are also nuclear velocity dependent (since it is proportional to  $\nabla_R$  operating on nuclear wave functions).

The adiabatic representation is defined by the requirement that the potential matrix  $U$  be diagonal for all  $\vec{R}$ . This representation employs for the electronic basis functions the eigenfunctions of  $H_{el}$ :

$$H_{el} \phi_k^a = W_k(\vec{R}) \phi_k^a ; \quad (\text{Ib.13})$$

the superscript  $a$  on the wave functions denoting adiabaticity. The effective potential energy surfaces governing nuclear motion in this representation are

$$U_{kk}^a(\vec{R}) = W_k(\vec{R}) . \quad (\text{Ib.14})$$

The only nonzero couplings in (Ib.9) are the nonadiabatic interactions  $T'_{ij}$  and  $T''_{ij}$ , hence the designation of adiabatic representation. Figure 1 shows a perspective view of the electronically adiabatic surfaces of the  $H^+D_2$  system with a translational degree ( $R$ ) and a vibrational degree ( $r$ ) of freedom [ $\vec{R}=(R,r)$ ].



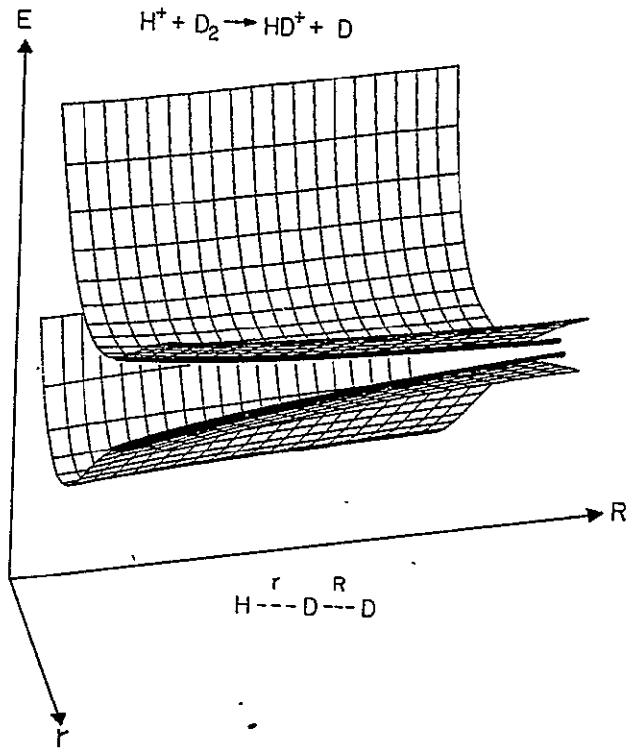


Fig. 1. A perspective view of the electronically adiabatic potential surfaces for  $H^+D_2$ .

Writing  $\frac{\hbar}{i} \nabla_{R_k}$  as  $\vec{p}^{(k)}$ , the matrix element  $\frac{\hbar}{i} \langle \phi_i | \nabla_{R_k} \phi_j \rangle$  in (Ib.11), can be written as

$$\frac{\hbar}{i} \langle \phi_i | \nabla_{R_k} \phi_j \rangle = \langle \phi_i | \vec{p}^{(k)} | \phi_j \rangle \equiv \vec{p}_{ij}^{(k)}. \quad (\text{Ib.15})$$

(Ib.11) can then be rewritten as

$$T'_{ij} = \sum_k \frac{1}{\mu_k} \vec{p}_{ij}^{(k)} \cdot \vec{p}^{(k)}. \quad (\text{Ib.16})$$

Hence in matrix notation

$$\tilde{T}' = \sum_k \frac{1}{\mu_k} \tilde{\vec{p}}^{(k)} \cdot \tilde{\vec{p}}^{(k)} \quad (\text{Ib.17})$$

Similarly  $\tilde{T}''$  can be written as

$$\tilde{T}'' = \sum_k \frac{1}{2\mu_k} (\tilde{\vec{p}}^{(k)} \cdot \tilde{\vec{p}}^{(k)} + \vec{p}^{(k)} \cdot \tilde{\vec{p}}^{(k)}) \quad (\text{Ib.18})$$

Comparison with (Ib.12) shows that (Ib.18) is indeed equivalent to it. Denoting the column matrix  $\chi_i$  by  $\tilde{\chi}$ , (Ib.9) can be rewritten in matrix form as

$$\begin{aligned} & \left[ \sum_k \left\{ \frac{1}{2\mu_k} \vec{p}^{(k)} \cdot \vec{p}^{(k)} + \frac{1}{2\mu_k} (\tilde{\vec{p}}^{(k)} \cdot \tilde{\vec{p}}^{(k)} + \vec{p}^{(k)} \cdot \tilde{\vec{p}}^{(k)}) + \frac{1}{\mu_k} \tilde{\vec{p}}^{(k)} \cdot \vec{p}^{(k)} \right\} \right. \\ & \left. + \underline{U}(\vec{R}) - \underline{1}E \right] \tilde{\chi}(\vec{R}) \equiv (\tilde{T} + \underline{U}(\vec{R}) - \underline{1}E) \tilde{\chi}(\vec{R}) = 0, \end{aligned} \quad (\text{Ib.19})$$

where  $\underline{1}$  is the unit matrix. We see that  $\tilde{T}$  can be identified as the generalized kinetic energy operator of the system. It is useful to write  $\tilde{T}$  as

$$\tilde{T} = \sum_k \frac{1}{2\mu_k} \tilde{\vec{p}}^{(k)} \cdot \tilde{\vec{p}}^{(k)}, \quad (\text{Ib.20})$$

where

$$\tilde{\vec{p}}^{(k)} \equiv \vec{p}^{(k)} + \underline{1}\vec{p}^{(k)} \quad (\text{Ib.21})$$

is the generalized momentum matrix of the  $k$  nuclear coordinate. Thus the matrices  $\tilde{\vec{p}}^{(k)}$  and  $\underline{U}(\vec{R})$  give complete dynamical information of the collision system. The diagonal elements of  $\tilde{\vec{p}}_{\ell m}^{(k)}$  vanish identically regardless of representation. This can be established by applying the operator  $\tilde{\vec{p}}^{(k)} = \frac{\hbar}{i} \nabla_{\vec{R}_k}$  to the ortho-

normality condition (Ib.5). This procedure also shows that  $\tilde{\vec{p}}^{(k)}$  is hermitian.

Nonadiabatic couplings tend to peak near avoided crossings, where  $U_{\ell\ell}^a - U_{mm}^a$  attains minimum values. Very often these regions arise because the adiabatic states are predominantly mixtures of two simple (molecular orbital or valence bond) structures (described by  $\phi_i$  and  $\phi_j$ ) whose corresponding potential energy surface ( $U_{ii}$  and  $U_{jj}$ ) cross. In one-dimensional (atom-atom) systems, if the crossing states are of the same symmetry, then the "non-crossing" rule requires that the adiabatic curves formed from them will exhibit an avoided crossing. The generalization of the non-crossing rule to systems with  $N$  internal nuclear

degrees of freedom can be stated as follows: the locus of points defined by the intersection of two N-dimensional exact adiabatic potential energy hypersurfaces corresponding to states of the same symmetry forms a hypersurface of at most N-2 dimensions.

During a molecular collision process, if the relative motion of the nuclei is sufficiently slow, they will tend to follow a single adiabatic potential energy surface, even near an avoided crossing. This is so because electronic motion always has time to adjust to the changing nuclear configuration. On the other hand, if the nuclei move very rapidly in the vicinity of an avoided crossing, the probability of nonadiabatic transition (moving from one adiabatic surface to another) will approach unity. This is due to insufficient time for the electrons to adjust their motion adiabatically to rapidly changing nuclear configurations. In the fast motion limit, therefore, the adiabatic representation may not be the most appropriate; and it may be more suitable to choose a representation in which the nonadiabatic couplings are minimal.

Representations which make use of electronic wave functions of desired characteristics (such as ionic or covalent) or those which minimize nonadiabatic couplings are in general known as diabatic representations - a term introduced originally by Lichten. Very often diabatic representations are chosen such that the matrices  $\tilde{p}^{(k)}$  vanish. In these representations transitions between surfaces are induced primarily by the off-diagonal elements  $U_{ij}$  of the Hamiltonian  $H_{el}$ . In the cases where these are small, the corresponding diabatic representation may be preferred over the adiabatic representation, even at low collision energies.

We will now illustrate the foregoing discussion with the simplest possible example of collision dynamics: the one-dimensional two-state problem. The matrix  $\tilde{T}$  (generalized kinetic energy) in (Ib.20) becomes

$$\tilde{T} = \frac{1}{2\mu} \tilde{p}^2 + \frac{1}{2\mu} (\tilde{p} \cdot \tilde{p} + \tilde{p}\tilde{p}) + \frac{1}{\mu} \tilde{p}p \quad (\text{Ib.22})$$

where all matrices are two-by-two and  $p = \frac{\hbar}{i} \frac{\partial}{\partial R}$ . We start with a diabatic representation in which  $\tilde{p}^d = 0$  (all nonadiabatic couplings vanish), and

$$\tilde{U}^d(R) = \begin{pmatrix} U_{11}^d(R) & U_{12}^d(R) \\ U_{12}^d(R) & U_{22}^d(R) \end{pmatrix}. \quad (\text{Ib.23})$$

To find the adiabatic representation, we have to transform  $\tilde{U}^d$  such that

$$\tilde{U}^a(R) = C^{-1}(R) \tilde{U}^d(R) C(R) \quad (\text{Ib.24})$$

becomes diagonal. The matrix that diagonalizes  $U^d(R)$  can be written

$$\tilde{C}(R) = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix}, \quad (\text{Ib.25})$$

where

$$\tan 2\alpha(R) = \frac{2U_{12}^d(R)}{[U_{22}^d(R) - U_{11}^d(R)]}. \quad (\text{Ib.26})$$

The adiabatic potential matrix  $\tilde{U}^a(R)$  is then

$$\tilde{U}^a(R) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tilde{U}(R) + \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} U(R) \quad (\text{Ib.27})$$

where

$$\tilde{U}(R) = \frac{1}{2} [U_{11}^d(R) + U_{22}^d(R)], \quad (\text{Ib.28})$$

$$U^2(R) = U_d^2(R) + [U_{12}^d(R)]^2, \quad (\text{Ib.29})$$

$$U_d(R) = \frac{1}{2} [U_{22}^d(R) - U_{11}^d(R)]. \quad (\text{Ib.30})$$

Of course the price we have to pay in using the adiabatic representation is that  $P^a \neq 0$  in general. If we represent the diabatic basis set by  $\phi_i^d$ , the adiabatic set will be given by

$$\phi_m^a = \sum_j C_{mj}^{-1} \phi_j^d. \quad (\text{Ib.31})$$

Hence 
$$P_{m\ell}^a = \langle \phi_m^a | \frac{\hbar}{i} \frac{\partial}{\partial R} | \phi_\ell^a \rangle = \frac{\hbar}{i} \sum_j C_{mj}^{-1} \frac{\partial}{\partial R} C_{\ell j}^{-1}; \quad (\text{Ib.32})$$

e.g. 
$$P_{12}^a = -\frac{\hbar}{i} \frac{\partial \alpha}{\partial R}.$$

We saw earlier that  $P_{ii}=0$  in any representation and  $\tilde{P}$  is always hermitian. Therefore,  $\tilde{P}^a$  in our example can be written

$$\tilde{P}^a(R) = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \hbar \frac{\partial \alpha(R)}{\partial R} . \quad (\text{Ib.33})$$

$\partial \alpha / \partial R$  can be obtained from differentiating (Ib.26):

$$\alpha' = \frac{\partial \alpha}{\partial R} = \frac{1}{2U^2} [U_d (U_{12}^d)' - U_{12}^d U_d'] . \quad (\text{Ib.34})$$

Recalling (Ib.22), we require the operators  $\tilde{P}^a \cdot \tilde{P}^a$ ,  $p \tilde{P}^a$  and  $\tilde{P}^a p$  operating on the nuclear wave functions  $\chi(R)$ . We will look at the effects of these in turn. First,  $\tilde{P}^a \cdot \tilde{P}^a$  is diagonal. Therefore, it does not couple the two adiabatic electronic states. Second,

$$\tilde{P}^a p = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \hbar^2 \alpha'(R) \frac{\partial}{\partial R} \quad (\text{Ib.35})$$

is the dominant nonadiabatic coupling matrix [which is also hermitian, since it involves  $\partial/\partial R$  acting on  $\chi_j(R)$ ]. Finally,

$$p \tilde{P}^a = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \hbar^2 \alpha''(R) \quad (\text{Ib.36})$$

is anti-hermitian. We will now consider the physical significance of the quantities  $\alpha'$  and  $\alpha''$  by examining the case of the Landau-Zener model. This model assumes straight-line potentials  $U_{11}^d(R)$  and  $U_{22}^d(R)$  and constant  $U_{12}^d$  near the crossing region. From (Ib.30) we see that  $U_d'$  is also constant near the crossing region. At the crossing point  $R_0$  itself,  $U_d(R)$  vanishes by definition and in general (regardless of the choice of dynamic models)

$$\alpha'(R_0) = - U_d'(R_0) / [2U_{12}^d(R_0)] . \quad (\text{Ib.37})$$

Hence in the Landau-Zener model  $\alpha'$  is constant throughout the vicinity of the crossing point, and the quantity  $\Delta R_0$  defined by

$$\Delta R_0 = 1/\alpha' \quad (\text{Ib.38})$$

is a length characterizing the effective width of the crossing region.  $\alpha''(R)$ , which governs the anti-hermitian nonadiabatic coupling (Ib.36), can be evaluated as [using (Ib.34)]:

$$\alpha'' = \frac{1}{2U^2} [U_d (U_{12}^d)'' - U_{12}^d U_d''] - \frac{2}{U^2} \alpha' [U_d U_d' + U_{12}^d (U_{12}^d)'] , \quad (\text{Ib.39})$$

which gives

$$\alpha''(R_0) = \frac{-U_d''(R_0)}{2U_{12}^d(R_0)} - \frac{U_d'(R_0)[U_{12}^d(R_0)]'}{[U_{12}^d(R_0)]^2} \quad (\text{Ib.40})$$

In the Landau-Zener model, this leads to  $\alpha''(R_0)=0$ . Thus we can just concentrate on the hermitian nonadiabatic coupling term. Since the off-diagonal elements  $U_{12}^d$  are diagonalized away in the adiabatic representation at the expense of the introduction of  $P^{ap}$ , the advantage of the adiabatic vs diabatic representations depends on the relative magnitudes of  $U_{12}^d$  and  $P^{ap}$ . We thus introduce a dimensionless constant reflecting this ratio:

$$\lambda_\ell(R) = \frac{\hbar \alpha'(R) v_\ell(R)}{2U_{12}^d(R)} \quad (\text{Ib.41})$$

where  $v_\ell(R)$  is a state-dependent nuclear velocity given by

$$\frac{1}{2} \mu v_\ell^2(R) = E - U_{\ell\ell}^d(R) \quad (\text{Ib.42})$$

and  $E$  is the total energy (kinetic + potential) of the collision system. At  $R_0$  (when  $v$  becomes state independent since  $U_{11}^d=U_{22}^d$ ) we then have

$$\lambda(R_0) = \frac{\hbar v(R_0)}{2U_{12}^d(R_0) \Delta R_0} = \frac{v(R_0)}{v_0} \quad (\text{Ib.43})$$

where

$$v_0 \equiv \frac{2U_{12}^d(R_0) \Delta R_0}{\hbar} \quad (\text{Ib.44})$$

is a characteristic velocity which also plays a prominent role in Landau-Zener transition probabilities (see Section IIa).  $v_0$  is then the critical velocity determining the suitability of adiabatic vs diabatic representations. If  $v(R) \gg v_0$ ,  $\lambda \gg 1$ , and (I.41) implies that  $U_{12}^d$  is insignificant compared to the strength of nonadiabatic couplings. Hence for high nuclear velocities, the diabatic representation would be more favorable. On the other hand, if  $v \ll v_0$ ,  $U_{12}^d$  exceeds the nonadiabatic couplings even at the crossing point, where they tend to be the strongest, and the diabatic representation would lose its advantage compared to the adiabatic. Far from the crossing region ( $R \rightarrow \infty$ ), we can assume that

$$U_{12}^d(\infty) = 0 \quad ,$$

$$\frac{\partial}{\partial R} U_{12}^d(\infty) = 0 \quad ,$$

$$U_d(\infty) = \text{const.}$$

$$\text{and} \quad U'_d(\infty) = 0, \quad (\text{Ib.45})$$

such that the logarithmic derivative of  $U_{12}^d$  tends to a finite limit

$$\lim_{R \rightarrow \infty} \frac{[U_{12}^d]'}{U_{12}^d} = k_{12}. \quad (\text{Ib.46})$$

Then, from (Ib.34)

$$\lim_{R \rightarrow \infty} \frac{\alpha'}{U_{12}^d} = \lim_{R \rightarrow \infty} \frac{(U_{12}^d)'}{2U_d U_{12}^d} = \frac{k_{12}}{2U_d(\infty)} \quad (\text{Ib.47})$$

and, using (Ib.41),

$$\lambda(\infty) = \frac{\hbar v(\infty)}{4U_d(\infty)}. \quad (\text{Ib.48})$$

Since  $\lambda(\infty) \gg 1$  for high velocities, (Ib.41) again shows that under these conditions, the diabatic representation is more favorable for large  $R$ . In view of the discussion above we can conclude that for large velocities, the diabatic representation is preferable for all  $R$ .

#### Ic. Quantum Mechanical Treatment of Nuclear Motion - Close Coupling

In the last subsection we have separated electronic from nuclear motions by appropriately choosing Born-Oppenheimer electronic basis functions. To deal with nuclear motion we must further separate the coordinates describing relative nuclear motion from those describing internal motion (vibration and rotation). Quantum mechanically this is usually done by expanding  $\chi_\ell(\vec{R})$  as [in analogy to (Ib.7)]

$$\chi_\ell(\vec{\rho}, \vec{R}') = \sum_{\alpha} u_{\ell\alpha}(\vec{\rho}) \xi_{\ell\alpha}(\vec{R}'; \vec{\rho}) \quad (\text{Ic.1})$$

where  $\vec{\rho}$  stands for the relative motion coordinates and  $\vec{R}'$  the internal motion (vibrational-rotational) coordinates.  $\xi_{\ell\alpha}$  is the nuclear motion wave function for the  $\alpha$  internal vibrational-rotational state of the  $\ell$  electronic state and, as written in (Ic.1), is taken to depend parametrically on  $\vec{\rho}$ . Similar to the case of purely electronic transitions, the nuclear wave functions  $u_{\ell\alpha}$  directly give S-matrix elements for transitions between electronic and internal nuclear states. To solve for  $u_{\ell\alpha}$ , we

have to substitute (Ic.1) into (Ib.9), or, equivalently, (Ib.19). First we write (assuming there is only one internal coordinate  $\vec{R}'$ )

$$T_R = -\frac{\hbar^2}{2\mu} \nabla_\rho^2 - \frac{\hbar^2}{2\mu'} \nabla_{R'}^2 \quad (\text{Ic.2})$$

where  $\mu$  and  $\mu'$  are reduced masses for the relative and internal motions respectively. (The case of many internal degrees of freedom will not affect the formal development of the coupled equations). Analogous to (Ib.11) and (Ib.12) we have

$$T'_{ij} = -\frac{\hbar^2}{2\mu} \langle \phi_i | \nabla_\rho \phi_j \rangle \cdot \nabla_\rho - \frac{\hbar^2}{2\mu'} \langle \phi_i | \nabla_{R'} \phi_j \rangle \cdot \nabla_{R'} \quad (\text{Ic.3})$$

$$T''_{ij} = -\frac{\hbar^2}{2\mu} \langle \phi_i | \nabla_\rho^2 \phi_j \rangle - \frac{\hbar^2}{2\mu'} \langle \phi_i | \nabla_{R'}^2 \phi_j \rangle \quad (\text{Ic.4})$$

Multiplying (Ib.9) by  $\xi_{i\alpha}$  and integrating over  $\vec{R}'$ , making use of the property (orthonormality of  $\xi_{i\alpha}$  for the same electronic state)

$$\int d^3 R' \xi_{i\alpha} \xi_{i\alpha'} = \delta_{\alpha\alpha'} \quad (\text{Ic.5})$$

we arrive at the coupled equations

$$\left( -\frac{\hbar^2}{2\mu} \nabla_\rho^2 - E \right) u_{i\alpha}(\vec{\rho}) = \sum_{j\alpha'} \Omega_{i\alpha, j\alpha'}(\vec{\rho}) u_{j\alpha'}(\vec{\rho}) \quad (\text{Ic.6})$$

where

$$\begin{aligned} \Omega_{i\alpha, j\alpha'} &= \int d^3 R' \xi_{i\alpha} (U_{ij} + T'_{ij} + T''_{ij}) \xi_{j\alpha'} \\ &- \frac{\hbar^2}{\mu} \left\{ \int d^3 R' \xi_{i\alpha} (\langle \phi_i | \nabla_\rho \phi_j \rangle + \delta_{ij} \nabla_\rho) \xi_{j\alpha'} \right\} \cdot \nabla_\rho \\ &- \delta_{ij} \frac{\hbar^2}{2} \int d^3 R' \xi_{i\alpha} \left( \frac{\nabla_\rho^2}{\mu} + \frac{\nabla_{R'}^2}{\mu'} \right) \xi_{j\alpha'} \quad (\text{Ic.7}) \end{aligned}$$

We note that  $\xi_{i\alpha}$  and  $\xi_{j\alpha}$  need not be orthogonal if  $i \neq j$ . The integral

$$\int d^3 R \xi_{i\alpha} \xi_{j\alpha'} \equiv \gamma_{i\alpha, j\alpha'} \quad (\text{Ic.8})$$

gives the overlap between internal nuclear wave functions on different electronic potential energy surfaces. The program of



close coupling quantum mechanical calculations is the solution of (Ic.6), for which several powerful algorithms have been developed. In principle (Ic.6) is capable of describing rotational, vibrational as well as electronic transitions. However, the problem may become prohibitively difficult as the number of open channels increases.

#### Id. Semiclassical S-Matrix Elements and the Stationary Phase Approximation

In this subsection we will present a formulation of the classical limit ( $\hbar \rightarrow 0$ ) of the S-matrix due to Miller (A complementary formulation has been carried out by Marcus.) This form for the S-matrix for molecular collisions takes advantage of the fact that heavy particle dynamics of the molecular collision system can be well treated by classical mechanics. We will first consider the case of electronically elastic (adiabatic) collisions in which the motion of nuclei follows a single electronically adiabatic surface  $U^a(\vec{R})$ . In Section III we will generalize our formulation to electronically nonadiabatic collisions based on a path integral formalism.

For the description of adiabatic motion we can use the Hamiltonian

$$H = \frac{p^2}{2\mu} + h(R') + V(R', \rho) \quad (\text{Id.1})$$

where the coordinates  $R'$  and  $\rho$  retain the same meaning as in the last subsection and  $P$  is the momentum operator canonically conjugate to  $\rho$ .  $V(R', \rho)$  is an interaction which vanishes as  $\rho \rightarrow \infty$ , and

$$h|n\rangle = \epsilon_n |n\rangle \quad (\text{Id.2})$$

defines the asymptotic ( $\rho \rightarrow \infty$ ) internal states  $|n\rangle$  with internal energies  $\epsilon_n$ . In a given electronically adiabatic collision process, we are interested in obtaining the transition amplitude between two internal states defined by  $h$ , i.e., the S-matrix element

$$S_{n_2, n_1}(E), \quad (\text{Id.3})$$

where  $E$  is the total energy of the collision system. We will first establish a relationship between the S-matrix element and the Green's function (Ia.20), which will then be computed in the classical limit to give an expression for the semiclassical S-matrix. To obtain  $G^+(E)$ , we first have to calculate  $G_0^+(E)$ , the unperturbed retarded Green's function corresponding to the Hamiltonian

$$H_0 = H - V \quad (\text{Id.4})$$

in the translational coordinate and internal quantum number representation  $|\rho, n\rangle$ . This is given by

$$\langle \rho_2, n_2 | G_0^+(E) | \rho_1, n_1 \rangle = \delta_{n_2 n_1} \left( \frac{-2\mu}{\hbar^2} \right) \frac{\sin(k_1 \rho_<)}{k_1} e^{ik_1 \rho_>} \quad (\text{Id.5})$$

$$\text{where} \quad k_1 = \left[ \frac{2\mu(E - \epsilon_{n_1})}{\hbar^2} \right]^{1/2} \quad (\text{Id.6})$$

and  $\rho_<(\rho_>)$  is the smaller (larger) of  $\rho_1$  and  $\rho_2$ . Substituting into (Ia.18) we have, for  $n_1 \neq n_2$ ,

$$\begin{aligned} \langle \rho_2, n_2 | G^+(E) | \rho_1, n_1 \rangle &= \int_0^\infty d\rho'_1 \int_0^\infty d\rho'_2 \langle \rho_2, n_2 | G_0^+(E) | \rho'_2, n_2 \rangle \\ &\times \langle \rho'_2, n_2 | T(E) | \rho'_1, n_1 \rangle \langle \rho'_1, n_1 | G_0^+(E) | \rho_1, n_1 \rangle . \end{aligned} \quad (\text{Id.7})$$

Hence

$$\begin{aligned} \lim_{\rho_1, \rho_2 \rightarrow \infty} \langle \rho_2, n_2 | G^+(E) | \rho_1, n_1 \rangle &= \lim_{\rho_1, \rho_2 \rightarrow \infty} \left( \frac{2\mu}{\hbar^2} \right)^2 \exp(ik_1 \rho_1 + ik_2 \rho_2) \\ &\times \langle k_2, n_2 | T(E) | k_1, n_1 \rangle \end{aligned} \quad (\text{Id.8})$$

$$\begin{aligned} \text{where } \langle k_2, n_2 | T | k_1, n_1 \rangle &= \int_0^\infty d\rho'_1 \int_0^\infty d\rho'_2 \frac{\sin k_2 \rho'_2}{k_2} \langle \rho'_2, n_2 | T(E) | \rho'_1, n_1 \rangle \\ &\times \frac{\sin k_1 \rho'_1}{k_1} . \end{aligned} \quad (\text{Id.9})$$

Since the T- and S-matrices are related by

$$S_{n_2, n_1} = \delta_{n_2 n_1} - 2i \left( \frac{2\mu}{\hbar^2} \right) (k_1 k_2)^{1/2} \langle k_2, n_2 | T(E) | k_1, n_1 \rangle , \quad (\text{Id.10})$$

we can identify the S-matrix in terms of  $G^+(E)$  as ( $n_1 \neq n_2$ )

$$\begin{aligned}
S_{n_2, n_1}(E) &= -\frac{i\hbar^2}{\mu} (k_1 k_2)^{1/2} \lim_{\rho_1, \rho_2 \rightarrow \infty} \exp(-ik_1 \rho_1 - ik_2 \rho_2) \\
&\times \langle \rho_2 n_2 | G^+(E) | \rho_1 n_1 \rangle = \lim_{\rho_1, \rho_2 \rightarrow \infty} \left( \frac{\hbar^2 k_1 k_2}{\mu^2} \right)^{1/2} \\
&\times \exp(-ik_1 \rho_1 - ik_2 \rho_2) \int_0^\infty dt \exp\left(\frac{iEt}{\hbar}\right) \langle \rho_2 n_2 | \exp\left(\frac{-iHt}{\hbar}\right) | \rho_1 n_1 \rangle
\end{aligned}$$

(Id.11)

where we have made use of (Id.20).

So far the treatment has been exactly quantum mechanical. In order to evaluate  $S_{n_2, n_1}$  in the classical limit, we use the classical Hamiltonian in (Id.11), which is given by [compare (Id.1)]

$$H(P, \rho, \vec{n}, \vec{q}) = \frac{P^2}{2\mu} + \varepsilon(\vec{n}) + V(\rho, \vec{n}, \vec{q}) \quad (\text{Id.12})$$

This Hamiltonian has been expressed in terms of the action-angle variables  $\{n_i\}$  and  $\{q_i\}$ ,  $i=1, \dots, N-1$ , where  $N$  is the total number of nuclear degrees of freedom. These variables describe internal motion classically and, in particular, the action variables  $\vec{n}$  are the classical counterpart of the quantum numbers for the internal degrees of freedom. WKB quantum conditions require that  $n_i$  be integers at asymptotic regions ( $\rho \rightarrow \infty$ ), and this forms the basis for the semiclassical description of the initial and final quantum states of the collision system.

In order to proceed further, we have to digress to present a result for the classical limit ( $\hbar \rightarrow 0$ ) Green's function in the coordinate representation:

$$\begin{aligned}
\langle q_2 | \exp\left[-\frac{iH(t_2 - t_1)}{\hbar}\right] | q_1 \rangle &= \left[ -\frac{\partial^2 \phi(q_2, q_1) / \partial q_2 \partial q_1}{2\pi i \hbar} \right]^{1/2} \\
&\times \exp\left[\frac{i\phi(q_2, q_1)}{\hbar}\right] \quad (\text{Id.13})
\end{aligned}$$

where  $\phi$  is the classical action, the time integral of the classical Lagrangian,

$$\phi(q_2, q_1) = \int_{t_1}^{t_2} dt \{p(t) \dot{q}(t) - H[p(t), q(t)]\} \quad (\text{Id.14})$$

and  $p, q$  are the canonically conjugate momentum and coordinate. The only approximation involved in the derivation of (Id.13) is the stationary phase approximation formula:

$$\int dx g(x) \exp \left[ \frac{if(x)}{\hbar} \right] \approx \sum_k g(x_k) \left[ \frac{2\pi i \hbar}{f''(x_k)} \right]^{1/2} \exp \left[ \frac{if(x_k)}{\hbar} \right] \quad (\text{Id.15})$$

where the points of stationary phase are given by

$$f'(x_k) = 0. \quad (\text{Id.16})$$

Since (Id.15) becomes exact as  $\hbar \rightarrow 0$ , one may say that classical mechanics is the stationary phase approximation of quantum mechanics.

Making use of (Id.13) in (Id.11) we have

$$\begin{aligned} S_{n_2, n_1}(E) &= \lim_{\rho_1, \rho_2 \rightarrow \infty} \left( -\frac{P_1 P_2}{\mu} \right)^{1/2} \exp \left[ \frac{i}{\hbar} (P_1 \rho_1 - P_2 \rho_2) \right] \\ &\times \int_0^\infty dt \left[ \frac{\partial^2 \phi(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t) / \partial (\rho_2 \vec{n}_2) \partial (\rho_1 \vec{n}_1)}{(-2\pi i \hbar)^N} \right]^{1/2} \\ &\times \exp \left[ \frac{i}{\hbar} [Et + \phi(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t)] \right] \quad (\text{Id.17}) \end{aligned}$$

where the action integral in the mixed representation  $(\rho, \vec{n})$  is

$$\phi(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t) = \int_{t_1}^{t_2} dt' [P(t') \dot{\rho}(t') - \vec{q}(t') \cdot \dot{\vec{n}}(t') - H(t')] , \quad (\text{Id.18})$$

$$t \equiv t_2 - t_1 ,$$

and the momenta  $P_1$  and  $P_2$ , with directions accounted for, are given by

$$P_1 = -\hbar k_1 ;$$

$$P_2 = -\hbar k_2 .$$

The stationary phase approximation (Id.15) is now invoked again to do the integral in (Id.17). First we note that

$$\frac{\partial \phi}{\partial t} (\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t) = - E(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t) \quad (\text{Id.19})$$

where  $E(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t)$  is the total energy for the trajectory with the indicated boundary conditions. It is distinct from the constant quantity appearing in the argument of  $S_{n_2, n_1}(E)$ . In fact, the stationary phase condition

$$-\frac{\partial}{\partial t} \phi(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t) \equiv E(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t) = E \quad (\text{Id.20})$$

defines the functional relationship between  $E$  and  $t$ . The stationary phase in the integrand of (Id.17) can now be written

$$\begin{aligned} \phi(\vec{n}_2, \vec{n}_1; E) &= P_1 \rho_1 - P_2 \rho_2 + Et - \int_{t_1}^{t_2} dt' [P(t') \dot{\rho}(t') - \vec{q}(t') \cdot \dot{\vec{n}}(t')] \\ &\quad - H(t')] = \int_{-\infty}^{\infty} dt [-\rho(t) \dot{P}(t) - \vec{q}(t) \cdot \dot{\vec{n}}(t)] , \end{aligned} \quad (\text{Id.21})$$

and

$$\begin{aligned} S_{n_2, n_1}(E) &= \left[ -\frac{P_1 P_2}{\mu^2} \frac{\partial t}{\partial E} \frac{\partial^2 \phi(\rho_2 \vec{n}_2, \rho_1 \vec{n}_1; t)}{\partial(\rho_2 \vec{n}_2) \partial(\rho_1 \vec{n}_1)} \right]^{1/2} (-2i\pi\hbar)^{N-1} \\ &\quad \times \exp \left[ \frac{i\phi(\vec{n}_2, \vec{n}_1; E)}{\hbar} \right] \end{aligned} \quad (\text{Id.22})$$

The pre-exponential derivative in (Id.22) is actually the determinant

$$\begin{vmatrix} \frac{\partial^2 \phi}{\partial \vec{n}_1 \partial \vec{n}_2} & \frac{\partial^2 \phi}{\partial \vec{n}_2 \partial \rho_1} \\ \frac{\partial^2 \phi}{\partial \rho_2 \partial \vec{n}_1} & \frac{\partial^2 \phi}{\partial \rho_2 \partial \rho_1} \end{vmatrix} \quad (\text{Id.23})$$

which can be shown to be (with some messy algebra):

$$\frac{\partial^2 \phi}{\partial(\rho_2 \vec{n}_2) \partial(\rho_1 \vec{n}_1)} = \frac{\mu^2}{P_1 P_2} \left( \frac{\partial t}{\partial E} \right)^{-1} \frac{\partial^2 \phi(\vec{n}_2, \vec{n}_1; E)}{\partial \vec{n}_2 \partial \vec{n}_1} . \quad (\text{Id.24})$$

The expression (Id.22) for the semiclassical S-matrix then simplifies to

$$S_{\vec{n}_2, \vec{n}_1}(E) = i \left[ \frac{\partial^2 \phi(\vec{n}_2, \vec{n}_1; E) / \partial \vec{n}_2 \partial \vec{n}_1}{(-2\pi i \hbar)^{N-1}} \right]^{1/2} \exp \left[ \frac{i \phi(\vec{n}_2, \vec{n}_1; E)}{\hbar} \right] \quad (\text{Id.25})$$

We can go one more step to simplify the pre-exponential factor. From (Id.21) we have

$$\phi(\vec{n}_2 \rho_2, \vec{n}_1 \rho_1; t) = \phi(\vec{n}_2, \vec{n}_1; E) + P_2 \rho_2 - P_1 \rho_1 - Et \quad (\text{Id.26})$$

and from (Id.18),

$$\frac{\partial \phi}{\partial \vec{n}_1} = \vec{q}_1 \quad (\text{Id.27})$$

Differentiating (Id.26) with respect to  $\vec{n}_1$ , we obtain

$$\begin{aligned} \frac{\partial \phi}{\partial \vec{n}_1}(\vec{n}_2, \vec{n}_1; E) &= \vec{q}_1 + \rho_1 \frac{\partial P_1}{\partial \vec{n}_1} \\ &= \vec{q}_1 - \hbar \rho_1 \frac{\partial k_1}{\partial \vec{n}_1} \\ &= \vec{q}_1 - \frac{\mu \rho_1}{P_1} \frac{\partial \epsilon(\vec{n}_1)}{\partial \vec{n}_1} \equiv \vec{q}_1' \quad (\text{Id.28}) \end{aligned}$$

where in the last equality we have used (Id.6). If we consider the time dependence of  $\vec{q}_1$  without the interaction potential in (Id.12), i.e., the time dependence in asymptotic regions, we see that (using Hamilton's equations)

$$\dot{\vec{q}}_1 = \frac{\partial H}{\partial \vec{n}_1} = \frac{\partial \epsilon(\vec{n}_1)}{\partial \vec{n}_1} \quad (\text{Id.29})$$

$$\dot{\rho}_1 = \frac{\partial H}{\partial P} = \frac{P_1}{\mu} \quad (\text{Id.30})$$

Hence

$$q(t_1) = \text{const} + \frac{\partial \epsilon(\vec{n}_1)}{\partial \vec{n}_1} t_1 \quad (\text{Id.31})$$

$$\rho(t_1) = \text{const} + \frac{P_1}{\mu} t_1, \quad (\text{Id.31})$$

and  $\vec{q}_1'$  as defined in (Id.28) does not have any asymptotic time dependence, that is, it has the "free" time dependence of  $\vec{q}(t)$  subtracted out. The pre-exponential factor of  $S_{n_2, n_1}$  is then given by

$$\frac{\partial^2 \phi(\vec{n}_2, \vec{n}_1, E)}{\partial \vec{n}_2 \partial \vec{n}_1} = \left( \frac{\partial \vec{q}_1'}{\partial \vec{n}_2} \right)_{\vec{n}_1} = \left[ \left( \frac{\partial \vec{n}_2}{\partial \vec{q}_1'} \right)_{\vec{n}_1} \right]^{-1} \quad (\text{Id.32})$$

Finally the S-matrix can be expressed most conveniently by

$$S_{\vec{n}_2, \vec{n}_1}(E) = i \left[ (-2\pi i \hbar)^{N-1} \left( \frac{\partial \vec{n}_2}{\partial \vec{q}_1'} \right)_{\vec{n}_1} \right]^{-1/2} \exp \left[ \frac{i \phi(\vec{n}_2, \vec{n}_1, E)}{\hbar} \right], \quad (\text{Id.33})$$

where  $\phi$  is given by (Id.21). In any application of (Id.33), we must determine classical trajectories specified by initial boundary conditions

$$\begin{aligned} \vec{n}(t_1) &\equiv \vec{n}_1 = \text{specified integers} \\ \rho(t_1) &= \text{asymptotically large} \\ P(t_1) &= -\{2\mu[E - \epsilon(\vec{n}_1)]\}^{1/2} \\ \vec{q}(t_1) &= \vec{q}_1' + \frac{\mu \rho(t_1)}{P(t_1)} \frac{\partial \epsilon(\vec{n}_1)}{\partial \vec{n}_1} \end{aligned} \quad (\text{Id.34})$$

and final conditions

$$\begin{aligned} \vec{n}(t_2) &\equiv \vec{n}_2 = \text{specified integers} \\ \rho(t_2) &= \text{asymptotically large} \\ P(t_2) &= \{2\mu[E - \epsilon(\vec{n}_2)]\}^{1/2} \\ \vec{q}(t_2) &= \text{anything} \end{aligned} \quad (\text{Id.35})$$

If there is more than one trajectory fitting the prescribed boundary conditions, (Id.33) must consist of a sum of terms, one for each such trajectory. To evaluate the derivatives  $\partial \vec{n}_2 / \partial \vec{q}_1'$ , we must integrate Hamilton's equations to obtain a function

$\vec{n}_2(\vec{q}_1', \vec{n}_1; E)$ , whose values, of course, need not be integers. We will then have to solve

$$\vec{n}_2 = \vec{n}_2(\vec{q}_1') \quad (\text{Id.36})$$

(with the arguments  $\vec{n}_1$  and  $E$  of  $\vec{n}_2$  suppressed) for the initial angle variables  $\vec{q}_1'$  which would lead to the prescribed final integral values for  $\vec{n}_2$ . (Id.36) is a set of  $N-1$  equations in the  $N-1$  unknowns  $\vec{q}_1'$ , and the pre-exponential factor  $\partial \vec{n}_2 / \partial \vec{q}_1'$  is in fact a determinant of partial derivatives, which are to be evaluated at the roots of (Id.36). Each set of roots  $\vec{q}_1'$  will then correspond to a distinct trajectory and will lead to a different  $\Phi$ .

## II. SPECIFIC THEORIES AND DYNAMICAL MODELS

In this section we will begin by studying simple dynamical models for nonadiabatic electronic transitions. We will consider low energy collisions such that the characteristic extent of nonadiabatic coupling is small. Under such circumstances the potential surfaces  $U_{ij}(\vec{R})$  and the nonadiabatic coupling matrix elements can very often be approximated by analytic functions of  $\vec{R}$ . Moreover, the transition can be considered as due solely to the coupling between two electronic states, thus the general multistate problem defined by (Ib.9) can be reduced to the relatively simple two-state problem. We will state our problem in terms of the semiclassical time-dependent formulation.

The Schrodinger equation to be solved is

$$H\psi(\vec{R}, \vec{r}; t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{R}, \vec{r}; t) \quad (\text{II.1})$$

where [compare with (Ib.7)]

$$\psi(\vec{R}, \vec{r}; t) = \sum_{\ell} \chi_{\ell}(\vec{R}; t) \phi_{\ell}(\vec{R}, \vec{r}) \quad (\text{II.2})$$

If  $\{\phi_{\ell}\}$  is chosen to be an adiabatic representation, (II.1) becomes

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + U_{ii}^a(R) \right\} \chi_i + \sum_{j \neq i} T_{ij} \chi_j = i\hbar \frac{\partial}{\partial t} \chi_i \quad (\text{II.3})$$

$$\text{where} \quad T_{ij} \equiv \langle \phi_i | -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \phi_j \rangle - \frac{\hbar^2}{\mu} \langle \phi_i | \frac{\partial}{\partial R} \phi_j \rangle \frac{\partial}{\partial R}, \quad (\text{II.4})$$

and a one-dimensional problem has been assumed. [It is seen that  $T_{ij} = T_{ij}^I + T_{ij}^{II}$ , on comparison with (Ib.11) and (Ib.12)]. The



$T_{ij}$  are, of course, the nonadiabatic couplings discussed in Section Ib.2.

So far, our time-dependent formulation is rigorously quantum mechanical, and (II.3) is equivalent to (Ib.9). The semiclassical viewpoint is introduced in assuming a classical trajectory

$$R = R(t) .$$

The electronic Hamilton  $H_{el}$  then becomes time-dependent through  $R(t)$ , and the electronic motion can be described by a time-dependent wave function  $\Phi(\vec{r};t)$  satisfying

$$H_{el}(\vec{r}, R(t))\Phi(\vec{r};t) = i\hbar \frac{\partial}{\partial t} \Phi(\vec{r};t) . \quad (II.5)$$

$\Phi$  can be expanded in terms of the  $\phi_i$ :

$$\Phi(\vec{r};t) = \sum_i a_i(t) \phi_i(R(t), \vec{r}) \exp\left\{-\frac{i}{\hbar} \int_0^t U_{ii}^a(R(t)) dt\right\} . \quad (II.6)$$

The nonadiabatic transition amplitudes, or S-matrix elements, are then determined by  $|a_n(t)|^2$ . Substitution of (II.6) into (II.5) gives

$$i\hbar \dot{a}_i = \sum_{j \neq i} C_{ij} \exp\left\{-\frac{i}{\hbar} \int_0^t dt (U_{jj}^a - U_{ii}^a)\right\} a_j \quad (II.7)$$

where the nonadiabatic coupling matrix elements are

$$C_{ij} \equiv \langle \phi_i | -i\hbar \partial \phi_j / \partial t \rangle . \quad (II.8)$$

For a two-state problem we have

$$i\hbar \dot{a}_1 = C_{12} \exp\left\{\frac{i}{\hbar} \int_0^t dt (U_{11}^a - U_{22}^a)\right\} a_2 , \quad (II.9a)$$

$$i\hbar \dot{a}_2 = C_{21} \exp\left\{\frac{i}{\hbar} \int_0^t dt (U_{22}^a - U_{11}^a)\right\} a_1 . \quad (II.9b)$$

The S-matrix element  $S_{2 \leftarrow 1}$  is given by

$$S_{2 \leftarrow 1} = |a_2(t \rightarrow \infty)|^2 \quad (II.10)$$

with the initial conditions

$$a_1(-\infty) = 1 , \quad a_2(-\infty) = 0 , \quad (II.11)$$

and the coupling  $C_{12}$  is assumed to be maximum at  $t=0$ .

### IIa. The Landau-Zener Model

It is often more convenient to formulate collision problems in the diabatic rather than the adiabatic representation (see discussion in Section Ib.2). The Landau-Zener model of nonadiabatic coupling between electronic states of the same symmetry, for instance, is formulated in terms of the diabatic representation of the electronic Hamiltonian,  $U^d$ , defined by

$$\begin{aligned} U_{11}^d &= \bar{U}(R_0) - F_1(R-R_0) \\ U_{22}^d &= \bar{U}(R_0) - F_2(R-R_0) \\ U_{12}^d &= a = \text{const.} \end{aligned} \quad (\text{IIa.1})$$

where 
$$\bar{U}(R_0) \equiv U_{11}^d(R_0) = U_{22}^d(R_0) \quad , \quad (\text{IIa.2})$$

$R_0$  being the point of intersection of the diabatic curves, and  $F_1, F_2$  are constants. The equation of the trajectory in the vicinity of  $R_0$  is approximated by a linear function of time:

$$R - R_0 = v_0 t \quad . \quad (\text{IIa.3})$$

From (Ib.27),  $U^a$  is then given by

$$U_{11}^a = \bar{U}(R_0) - \frac{1}{2}(F_1+F_2)(R-R_0) - U(R) \quad (\text{IIa.4a})$$

$$U_{22}^a = \bar{U}(R_0) - \frac{1}{2}(F_1+F_2)(R-R_0) + U(R) \quad (\text{IIa.4b})$$

where 
$$4U^2(R) = \{\Delta F(R-R_0)\}^2 + 4a^2 \quad , \quad \Delta F = |F_1 - F_2| \quad . \quad (\text{IIa.5})$$

Analogous to the derivation of (Ib.32), we obtain

$$C_{12} = \hbar \partial \alpha / \partial t \quad . \quad (\text{IIa.6})$$

where  $\alpha$  is defined in (Ib.26). Using (Ib.34) in which ' means  $\partial/\partial t$ , (IIa.6) reduces to

$$c_{12} = \frac{i\hbar a(\Delta F)v_0}{\{\Delta F(v_0 t)\}^2 + 4a^2} . \quad (\text{IIa.7})$$

The exact solution of (II.9) using (IIa.4) and (IIa.7) has been carried out by Zener, and it is found that, for a 'once passage' through the nonadiabatic coupling region, the S-matrix is given by

$$|s_{2 \leftarrow 1}|^2 = |a_2(\infty)|^2 = \exp \left[ \frac{-2\pi a^2}{v_0 \hbar \Delta F} \right] . \quad (\text{IIa.8})$$

As discussed in the previous section, it is thus seen that when the velocity  $v_0$  is small, the nonadiabatic transition probability is also small. On the other hand, for  $v_0$  large,  $S_{2 \leftarrow 1}$  tends to unity, meaning that the colliding particles tend to follow the diabatic path.

#### IIb. The Demkov Model

In this model  $\tilde{U}^d(R)$  is given by

$$U_{22}^d(R) = \frac{\Delta}{2} = \text{const} , \quad U_{11}^d(R) = -\frac{\Delta}{2} , \quad (\text{IIb.1})$$

$$U_{12}^d(R) = A \exp(-\lambda R) , \quad (\text{IIb.2})$$

and the straight-line trajectory  $R(t)=v_0 t$  is also employed. Transforming to the adiabatic representation, we have

$$U_{11}^a(R) = -\frac{1}{2}[\Delta^2 + 4A^2 \exp(-2\lambda R)]^{1/2} \quad (\text{IIb.3a})$$

$$U_{22}^a(R) = \frac{1}{2}[\Delta^2 + 4A^2 \exp(-2\lambda R)]^{1/2} . \quad (\text{IIb.3b})$$

At asymptotic regions  $U_{11}^a(R) \rightarrow U_{11}^d(R)$  and  $U_{22}^a(R) \rightarrow U_{22}^d(R)$ . Hence in this case, opposite to the Landau-Zener model, the non-adiabatic transition amplitudes are the same as the diabatic ones. Expanding  $\Phi(\vec{r};t)$  in the diabatic basis set  $\{\phi_i^d\}$ :

$$\Phi(\vec{r};t) = \sum_i b_i(t) \phi_i^d(R(t), \vec{r}) \exp\left\{-\frac{i}{\hbar} \int_0^t dt U_{ii}^d(R(t))\right\} , \quad (\text{IIb.4})$$

we obtain, analogous to (II.9), the set of coupled equations

$$i\hbar \dot{b}_1 = U_{12}^d \exp\left\{\frac{i}{\hbar} \int_0^t dt (U_{11}^d - U_{22}^d)\right\} b_2 , \quad (\text{IIb.5a})$$

$$ib_2 = U_{21}^d \exp\left\{\frac{i}{\hbar} \int^t dt (U_{22}^d - U_{11}^d)\right\} b_1 . \quad (\text{IIb.5b})$$

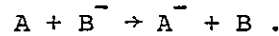
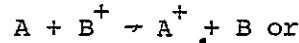
If we use the initial conditions

$$b_1(-\infty) = 1 , b_2(-\infty) = 0 , \quad (\text{IIb.6})$$

the 'once passage' S-matrix element or transition probability is given by  $|b_2(+\infty)|^2$ . The exact solution of (IIb.5) using (IIb.1) and (IIb.2), as worked out by Demkov, is given by

$$\begin{aligned} S_{2 \leftarrow 1} = |b_2(+\infty)|^2 &= \text{sech}^2 \left( \frac{\pi \Delta}{2 \hbar \lambda v_0} \right) \sin^2 \left( \frac{1}{\hbar} \int_{-\infty}^{\infty} dt U_{12}^d(R(t)) \right) \\ &= \sin^2 \left( \frac{2A}{\hbar \lambda v_0} \right) \text{sech}^2 \left( \frac{\pi \Delta}{2 \hbar \lambda v_0} \right) . \end{aligned} \quad (\text{IIb.7})$$

The Demkov model and the Demkov formula (IIb.7) is widely used to describe charge transfer processes of the type



### IIc. Stuckelberg Theory - Curve-Crossing Problems

In the diabatic representation (in which all nonadiabatic couplings vanish) the coupled equations of motion for the one-dimensional two-state problem are

$$\chi_1'' + \bar{k}_1^2(R) \chi_1 = \alpha(R) \chi_2 \quad (\text{IIc.1a})$$

$$\chi_2'' + \bar{k}_2^2(R) \chi_2 = \alpha(R) \chi_1 \quad (\text{IIc.1b})$$

$$\text{where} \quad \bar{k}_{1,2}^2 = \frac{2\mu}{\hbar^2} (E - U_{11,22}^d) , \quad (\text{IIc.2})$$

$$\alpha = \frac{2\mu}{\hbar^2} U_{12}^d \quad (\text{IIc.3})$$

and "denotes second derivative with respect to R. (IIc.1) is often used to describe collision dynamics with curve crossing, i.e., when  $U_{11}^d(R)$  and  $U_{22}^d(R)$  intersect at some point. The Stuckelberg method to solve these equations is based on semi-classical phase integrals and their analytic continuation in the

complex R plane. For unit amplitude entrance on channel 1, (IIc.1) must be solved subject to the boundary conditions

$$\chi_1(R)_{R \rightarrow \infty} e^{i\bar{k}_1(\infty)R} - S_{11} e^{i\bar{k}_1(\infty)R} \quad (\text{IIc.4a})$$

$$\chi_2(R)_{R \rightarrow \infty} - S_{12} e^{i\bar{k}_2(\infty)R} \quad (\text{IIc.4b})$$

where  $S_{11}$  and  $S_{12}$  are the scattering matrix elements.

The procedure of Stuckelberg to solve the equations is as follows. First one eliminates  $\chi_2$  from (IIc.1) to obtain a fourth order differential equation for  $\chi_1$ . A solution of the form

$$\chi_1 = \exp\left[\frac{1}{\hbar} S_0 + S_1 + \hbar S_2 + \dots\right] \quad (\text{IIc.5})$$

is then substituted into the fourth order equation to obtain equations for  $S_0, S_1, \dots$  when coefficients of the various powers of  $\hbar$  are separately equated to zero. Keeping only  $S_0$  and  $S_1$  one can arrive at the general WKB solutions for  $\chi_1$  and  $\chi_2$ . The solutions thus found are observed to have singularities at  $R_*$  which satisfies

$$(U_{22}^d - U_{11}^d)^2 + 4(U_{12}^d)^2 = 0. \quad (\text{IIc.6})$$

$R_*$  is in general complex and (IIc.6) implies that  $R_*^*$  is also a solution. The WKB forms  $\chi_1$  and  $\chi_2$  then cannot be used in the neighborhood of  $R_*$ , including the immediately adjacent real axis. It is, however, desirable to consider the approximate solutions  $\chi_{1,2}$  as analytic in sufficiently remote regions from the conjugate pair  $R_*$  and  $R_*^*$  so that  $\chi_{1,2}$  for  $R \gg \text{Re} R_*$  can be joined smoothly to  $\chi_{1,2}$  for  $R_1, R_2 \ll R \ll \text{Re} R_*$  ( $R_{1,2}$  being turning points) by tracing the WKB solutions along a contour remote from the neighborhood of  $R_*$  and  $R_*^*$ . Any contour chosen will invariably pass through the so-called Stokes lines, which are defined by

$$\text{Re} \int_{R_*}^R dR (k_1 - k_2) = 0 \quad (\text{IIc.7})$$

where 
$$k_{1,2}^2 = \frac{2\mu}{\hbar^2} (E - W_{1,2}) \quad (\text{IIc.8})$$

and  $W_{1,2}$  are the adiabatic curves obtained by diagonalizing  $U^d$ . The WKB solutions consist of dominant and subdominant solutions in the complex R plane. As one crosses a Stokes line the co-

efficient of the subdominant solution must change discontinuously in order for the solutions to join. This is known as the Stokes phenomenon, and one can say that a nonadiabatic transition is the physical manifestation of the Stokes phenomenon.

This connection procedure determines the coefficients of the WKB solutions whose asymptotic forms lead directly to the S-matrix. If there is only one region of nonadiabaticity (in which the WKB solutions are not valid), then there will be two crossing encounters due to the fact that this region is passed twice, once on the way in and once on the way out. Stuckelberg's solution for the S-matrix is given in this case by

$$S_{i,j} = (P_{i,j}^I)^{1/2} \exp(i\phi_{i,j}^I) + (P_{i,j}^{II})^{1/2} \exp(i\phi_{i,j}^{II}) \quad (\text{IIc.9})$$

for  $i,j=1,2$ , where  $W_1$  is chosen to be the lower adiabatic curve, the  $\phi$ 's are the WKB phase integrals (i.e., classical action integrals), the  $P$ 's are transition probabilities; and I and II refer to the two crossing encounters and thus to the two different classical trajectories that contribute to the  $i \rightarrow j$  nonadiabatic transition. The various quantities in (IIc.9) are given below:

$$\phi_{1,1}^I = \lim_{R \rightarrow \infty} 2(\xi - k_1 R + \int_{R_1}^R dR' k_1(R')) , \quad (\text{IIc.10a})$$

$$\phi_{1,1}^{II} = \lim_{R \rightarrow \infty} 2(\xi - k_1 R + \int_{R_2}^{\text{Re}R_*} dR' k_2(R') + \int_{\text{Re}R_*}^R dR' k_1(R')) , \quad (\text{IIc.10b})$$

$$\begin{aligned} \phi_{1,2}^I = \phi_{2,1}^I = \lim_{R \rightarrow \infty} (\xi - k_1 R - k_2 R + \int_{\text{Re}R_*}^R dR' k_1(R') + \int_{\text{Re}R_*}^R dR' k_2(R') \\ + 2 \int_{R_2}^{\text{Re}R_*} dR' k_2(R')) , \quad (\text{IIc.10c}) \end{aligned}$$

$$\begin{aligned} \phi_{1,2}^{II} = \phi_{2,1}^{II} = \lim_{R \rightarrow \infty} (-\xi - k_1 R - k_2 R + \int_{\text{Re}R_*}^R dR' k_1(R') + \int_{\text{Re}R_*}^R dR' k_2(R') \\ + 2 \int_{R_1}^{\text{Re}R_*} dR' k_1(R')) , \quad (\text{IIc.10d}) \end{aligned}$$

$$\phi_{2,2}^I = \lim_{R \rightarrow \infty} 2(\xi - k_2 R + \int_{R_2}^R dR' k_2(R')) , \quad (\text{IIc.10e})$$

$$\phi_{2,2}^{II} = \lim_{R \rightarrow \infty} 2(\xi - k_2 R + \int_{R_1}^{ReR_*} dR' k_1(R') + \int_{ReR_*}^R dR' k_2(R')) , \quad (IIc.10f)$$

$$P_{1,1}^I = P_{2,2}^I = (1-p)^2 , \quad (IIc.11a)$$

$$P_{1,1}^{II} = P_{2,2}^{II} = p^2 , \quad (IIc.11b)$$

$$P_{1,2}^I = P_{1,2}^{II} = P_{2,1}^I = P_{2,1}^{II} = p(1-p) , \quad (IIc.11c)$$

$$\text{where} \quad p = \exp(-2\delta) \quad (IIc.12)$$

is the local nonadiabatic transition probability and

$$\delta = i \int_{R_*}^{R_*} dR [k_2(R) - k_1(R)] = 2i \int_{ReR_*}^{R_*} dR [(k_2(R) - k_1(R))] . \quad (IIc.13)$$

In (IIc.10),  $k_i = k_i(\infty)$  and the phase factor  $\xi$  is given by (not originally given by Stuckelberg in this form)

$$\xi = \delta \ln \delta - \delta - \arg \Gamma(i\delta) - \frac{\pi}{4} . \quad (IIc.14)$$

For  $\delta \ll 1$ ,  $\xi \sim \frac{\pi}{4}$  and for  $\delta \gg 1$ ,  $\xi \sim -1/12\delta$ .

Interference between the two terms in (IIc.9) leads to oscillatory behavior of  $|S_{i,j}|^2$  as a function of  $E$ . This phenomenon is known as Stuckelberg oscillations. For example, considering the  $1 \rightarrow 2$  transition, we have

$$|S_{1,2}|^2 = 2p(1-p) [1 + \cos(\xi + A - B)] , \quad (IIc.15)$$

$$\text{where} \quad A = \int_{R_2}^{ReR_*} dR' k_2(R') , \quad (IIc.16a)$$

$$B = \int_{R_1}^{ReR_*} dR' k_1(R') . \quad (IIc.16b)$$

#### IIId. Tully-Preston Surface-Hopping Trajectory (SHT) Theory

The SHT approach is basically a classical trajectory approach in which nuclear motion is treated completely classically. Classical trajectories are propagated on the entrance

(initial) potential surface until an avoided surface crossing or other point of large nonadiabatic interaction is reached. A relation defining these avoided crossing seams have to be found for each problem:

$$S(\vec{R}) = 0 . \quad (\text{IIId.1})$$

A probability of switching to another surface  $P(\vec{R}, \dot{\vec{R}})$  is then computed and the trajectory branches. One branch, with the weight  $(1-P)$ , is resumed on the old surface, whereas a new branch, with the weight  $P$ , is resumed on the new potential surface, with a slight velocity correction. More branching will occur if the branched trajectories subsequently encounter the avoided crossing seam again, and at each encounter, a surface-hopping probability has to be determined.

The switching probabilities at each hopping encounter are calculated by integrating the coupled equations (II.9). For instance, if a trajectory is initially propagated on the adiabatic surface 1, then  $P = |a_2|^2$  is obtained by integrating (II.9) over the entire nonadiabatic coupling region. The solution obtained would, of course, depend on the choice of the classical trajectory  $\vec{R}(t)$  used in the  $R$ -dependent quantities in (II.9), which in turn depends on the choice of the potential (either  $U_{11}^a$  or  $U_{22}^a$ ) used for its determination. However, it has been found that for many triatomic systems of interest, especially the  $H_3^+$  system, the choice of the effective potential for the determination of  $\vec{R}(r)$  in (II.9) has relatively little effect on its solution, and very often the solutions given by the different choices can be approximated by the Landau-Zener formula with appropriate parameters. Furthermore the transition probability depends almost entirely on the component of velocity perpendicular to the avoided crossing seam.

An important requirement of the model is a prescription for changing velocities to conserve angular momentum and energy when a surface hop occurs. Since the perpendicular (to the seam) component of the velocity is most effective in nonadiabatic coupling, velocity corrections are usually applied to this component only. These corrections reflect the energy defect of the adiabatic surfaces on the seam at the site of hop.

Tully and Preston have obtained classical branching trajectories for the linear  $H^+ + D_2$  system using the surface hopping model as described and compared them with trajectories obtained from an effective potential given by

$$W_{\text{eff}}(\vec{R}) = |a_1|^2 W_1(\vec{R}) + |a_2|^2 W_2(\vec{R}) . \quad (\text{IIId.2})$$

If the entrance channel is on  $W_1$ , they observed that  $|a_2|^2$ , calculated by (II.9), was essentially zero except in the immediate neighborhood of the avoided crossing seam. In other regions, the trajectories determined from  $W_{\text{eff}}$  were nearly superimposable



on those determined from  $W_1(\vec{R})$ . Near the seam regions, however, the branched trajectories were significantly different from those determined from  $W_{\text{eff}}$ . Hence they concluded that, below a certain energy threshold, the probability of nonadiabatic transitions and the magnitude of nonadiabatic corrections to the potential [given by (IIId.2)] were both negligible except in regions near the avoided crossing seam.

There is one important difference between the SHT model and the semiclassical S-matrix theory introduced earlier (and which will be generalized to include nonadiabatic transitions in Section III). The SHT theory adds probabilities (rather than probability amplitudes) for different trajectories and hence is incapable of producing interference effects leading to resonances. This defect, however, may be unimportant when a large number of initial vibrational and rotational phases have to be averaged over, since the averaging process would serve to wash out the interference effects.

#### IIe. The Meyer-Miller Treatment of Classical Electronic Degrees of Freedom

Even though semiclassical methods have been largely successful in the treatment of molecular collision processes, their formulations are plagued by a fundamental shortcoming - electronic and nuclear degrees of freedom are not treated on the same dynamical footing. Since it is never seriously doubted that classical mechanics can be applied safely to nuclear motion, some attempts have been made to redress the situation by advancing schemes to treat electronic motion by classical degrees of freedom also. These attempts by no means aim at reducing electronic motion to the tempting framework of classical particles orbiting around the nucleus. One has rather to search for the right classical dynamical variables which will describe the relevant aspects of electronic motion in molecular collision dynamics. For this purpose we will present a recent formulation due to Meyer and Miller.

To motivate the choice of a suitable set of classical electronic degrees of freedom we will first formulate the general  $N$  electronic-state problem in the diabatic representation. The semiclassical description introduced at the beginning of Section II [assigning a specific classical trajectory  $\vec{R}=\vec{R}(t)$ ] leads to the set coupled equations

$$\dot{\alpha}_i = -\frac{i}{\hbar} \sum_j \alpha_j(t) U_{ij}^d(\vec{R}(t)), \quad i,j=1,\dots,N \quad (\text{IIe.1})$$

for the expansion coefficients of the electronic wave function

$$\Phi(r, R(t)) = \sum_i \alpha_i(t) \phi_i(r, R(t)) \quad (\text{IIe.2})$$

which satisfies the time-dependent electronic Schrödinger equation

$$H_{el}(r, R) \Phi = i \hbar \partial \Phi / \partial t. \quad (\text{IIe.3})$$

[Compare (IIb.5). Knowledge of  $\alpha_i(t)$  then gives directly transition amplitudes for electronic transitions between the states  $\phi_i$ . (In this subsection we limit ourselves to one-dimensional nuclear motion.)

One of the ways to assign the trajectory  $R(t)$  in (IIe.1) is to assume that nuclei motion follows a force field determined by Ehrenfest's theorem:

$$\begin{aligned} p \equiv \mu \ddot{R}(t) &= - \langle \Phi | \frac{\partial H_{el}(r, R)}{\partial R} | \Phi \rangle \\ &= - \sum_{ij} \alpha_i^*(t) d_j(t) \frac{\partial}{\partial R} U_{ij}^d(R). \end{aligned} \quad (\text{IIe.4})$$

Since the  $\alpha$ 's are unknowns in (IIe.4), this equation has to be adjoined to (IIe.1) to form a set of  $N+1$  equations for the solution of the  $N+1$  unknowns  $\alpha_i(t)$  and  $R(t)$ . Other choices of trajectories can be made (for example, as in the SHT model, in which  $R(t)$  is determined by the adiabatic potentials or  $W_{eff}$ ), but in any case, a single unique classical trajectory is used which is independent of the final electronic state, a clearly dynamically inconsistent situation. (In fact, this is one of the formal weaknesses of the SHT approach).

The Meyer-Miller approach consists in searching for a set of classical electronic degrees of freedom which would lead to Hamilton's equations of motion completely equivalent to (IIe.2) plus the Ehrenfest trajectory. Yet the boundary conditions of these Hamilton's equations, unlike those of the time-dependent semiclassical treatment, would be dynamically consistent, since electronic transitions now correspond to different initial and final values for certain of the classical electronic degrees of freedom, and different transitions entail different classical trajectories. These transitions can be conveniently and unambiguously described by the semiclassical S-matrix formulation of Section Id.

The sought-for classical electronic degrees of freedom are related to the  $\alpha_i(t)$  by

$$\alpha_i(t) = \sqrt{n_i(t)} \exp[-iq_i(t)] \quad (\text{IIe.5})$$

The  $n_i$  and  $q_i$  are analogous to those introduced in Section Id for

the description of internal nuclear motion and can be correspondingly considered as electronic action and angle variables. The classical Hamiltonian  $H_{el}(\vec{n}, \vec{q}; t)$  is then given by

$$\begin{aligned} H_{el}(\vec{n}, \vec{q}; t) &= \langle \Phi | H_{el}(\vec{r}, R(t)) | \Phi \rangle \\ &= \sum_{ij} \alpha_i^* \alpha_j U_{ij}^d(R(t)) , \end{aligned} \quad (II.6)$$

that is,

$$H_{el}(\vec{n}, \vec{q}; t) = \sum_{ij} \sqrt{n_i n_j} \exp\{i(q_i - q_j)\} U_{ij}^d(R(t)) . \quad (IIe.7)$$

Hamilton's equations for  $n_i$  and  $q_i$  are then given by

$$\dot{q}_i = \frac{\partial H_{el}(\vec{n}, \vec{q}; t)}{\partial n_i} , \quad (IIe.8a)$$

$$\dot{n}_i = - \frac{\partial H_{el}(\vec{n}, \vec{q}; t)}{\partial q_i} .$$

The full classical Hamiltonian becomes

$$H(p, R, \vec{n}, \vec{q}) = \frac{p^2}{2\mu} + \sum_{ij} \sqrt{n_i n_j} \exp\{i(q_i - q_j)\} U_{ij}^d(R) , \quad (IIe.9)$$

and Hamilton's equations for the canonical variables  $R, p, \vec{n}, \vec{q}$  are

$$\dot{R}(t) = \frac{\partial H}{\partial p} = \frac{p}{\mu} , \quad (IIe.10a)$$

$$\dot{p}(t) = - \frac{\partial H}{\partial R} = - \sum_{ij} \sqrt{n_i n_j} \exp\{i(q_i - q_j)\} \frac{\partial}{\partial R} U_{ij}^d(R) , \quad (IIe.10b)$$

$$\dot{q}_i(t) = \frac{\partial H}{\partial n_i} = \sum_j \sqrt{\frac{n_j}{n_i}} \operatorname{Re}[\exp\{i(q_i - q_j)\} U_{ij}^d] , \quad (IIe.10c)$$

$$\dot{n}_i(t) = \frac{\partial H}{\partial q_i} = \sum_j 2\sqrt{n_i n_j} \operatorname{Im}[\exp\{i(q_i - q_j)\} U_{ij}^d] . \quad (IIe.10d)$$

(IIe.10c) and (IIe.10d) can be shown to be equivalent to (IIe.1) if (IIe.5) is used in the latter. Furthermore (IIe.10b) is none other than (IIe.4), the Ehrenfest trajectory equation. Hence the goal of the Meyer-Miller program is achieved by the introduction

of the classical electronic degrees of freedom specified by (IIe.5).

As an example we consider the two-electronic-state problem. The classical electronic Hamiltonian (IIe.7) is given by

$$H_{el}(n_1, n_2, q_1, q_2) = n_1 U_{11}^d + n_2 U_{22}^d + 2\sqrt{n_1 n_2} U_{12}^d \cos(q_2 - q_1) . \quad (\text{IIe.11})$$

Making a canonical transformation to the new set of variables

$$\begin{aligned} n'_1 &= n_1 + n_2 = 1 \quad (\text{conservation of electronic probability}) \\ n'_2 &= n_2 , \\ q'_1 &= q_1 , \\ q'_2 &= q_2 - q_1 , \end{aligned} \quad (\text{IIe.12})$$

the two-state Hamiltonian reduces to one with only one degree of freedom  $(n'_2, q'_2) \equiv (n, q)$ ,

$$H_{el}(n, q) = (1-n)U_{11}^d + nU_{22}^d + 2\sqrt{n(1-n)} U_{12}^d \cos q . \quad (\text{IIe.13})$$

However, to make the boundary conditions amenable to classical treatment so that  $n(t_2) \equiv n_2$  is a function of  $q(t_1) \equiv q_1$ , we have to introduce the Langer-modified Hamiltonian

$$H_{el}^L(n, q) = (1-n)U_{11}^d + nU_{22}^d + 2\sqrt{n + \frac{1}{2}} \sqrt{\frac{3}{2} - n} U_{12}^d \cos q . \quad (\text{IIe.14})$$

Electronic transitions are then represented by the boundary conditions  $n(t_1) \equiv n_1 = 0$ ,  $n_2 = 1$ . To compute the S-matrix given by (Id.33), we have to solve the following equation for  $q_1$

$$n_2(q_1) = 1 \quad (\text{IIe.15})$$

and each root will give rise to a separate term in (Id.33).

### III. THE MILLER-GEORGE THEORY OF ELECTRONIC TRANSITIONS IN LOW ENERGY MOLECULAR COLLISIONS

In Section I we have introduced the semiclassical S-matrix for electronically adiabatic collisions in which electronic coordinates do not enter into the picture at all. Transitions between internal states of nuclear motion are described within the framework of classical degrees of freedom (action and angle variables) whose boundary values are quantized. In Section

II various ways to deal with nonadiabatic transitions are considered, some based on specific dynamical models, such as the Landau-Zener model, while others, such as the SHT treatment, are built on somewhat dynamically ill-defined boundary conditions, despite successes in many applications. The Meyers-Miller formalism attempts to put everything on firm grounds with the bold step of introducing classical electronic coordinates to complement the classical nuclear ones. This approach, though intellectually challenging and showing great promise, is as yet relatively undeveloped in its applicational aspects. In this section we retreat one step from the Meyers-Miller formalism, as it were, and discuss a treatment of nonadiabatic transitions due to Miller and George, which makes use of quantum mechanical electronic and classical nuclear degrees of freedom. Though suffering from the undesirable feature of having to mix classical and quantum mechanics, this formalism leads to a quite aesthetically appealing interpretation: all dynamics, including nonadiabatic transitions, is essentially described by classical motion of the nuclei on electronically adiabatic potential energy surfaces. Nonadiabatic motion is described by the analytic continuation of classical mechanics into complex coordinate regions. Hence all dynamical information is contained in the analytic structure of the adiabatic potential surfaces, and nonadiabatic coupling matrix elements, while centrally important in quantum mechanical treatments, do not enter explicitly into this formulation. Transitions between internal nuclear states are handled in the same way as described in Section Id.

### IIIa. The Feynman Propagator Approach

In our formulation of the S-matrix in Section Id, (Id.13) was the starting point. There we noted that this equation results from the stationary phase approximation of the Green's function propagator  $\langle q_2 | \exp[-iH(t_2-t_1)/\hbar] | q_1 \rangle$ , which is equivalent to the choice of a particular trajectory,  $q(t)$ , for the nuclear coordinate  $q$ . This particular trajectory is the one obtained from the solution of Hamilton's equations, and is thus called a classical trajectory. In the treatment of a problem involving electronic coordinates, we will be interested in the more generalized propagator in coordinate representation

$$\langle q_2, x_2 | \exp[-iH(t_2-t_1)/\hbar] | q_1, x_1 \rangle \quad (\text{IIIa.1})$$

where  $x_2, x_1$  are the collective electronic coordinates at  $t_2$  and  $t_1$  respectively.  $q$  denotes the collective nuclear coordinates. It was Pechukas who first developed the idea of building a formalism to treat molecular collisions involving electronic transitions based on the propagator (IIIa.1). Instead of starting midway to write down the stationary phase approximation for it, we begin with Feynman's path integral expression:

$$\begin{aligned}
& \langle q_2 x_2 | \exp \left( \frac{-iH(t_2 - t_1)}{\hbar} \right) | q_1 x_1 \rangle \\
&= \int_{q_1}^{q_2} Dq \int_{x_1}^{x_2} Dx \exp \left\{ \frac{i}{\hbar} \int_{t_1}^{t_2} dt \left[ \frac{1}{2} \mu \dot{q}^2 + T_x - V(x, q) \right] \right\} ,
\end{aligned}
\tag{IIIa.2}$$

where the path integrals are over all electronic and nuclear trajectories  $x(t)$  and  $q(t)$  that connect  $(x_1, q_1)$  at  $t_1$  and  $(x_2, q_2)$  at  $t_2$ , and  $T_x$  is the electronic kinetic energy. One can imagine doing the electronic path integral first (although in practice its actual evaluation is never carried out) and write

$$\begin{aligned}
\langle q_2 x_2 | \exp \left( \frac{-iH(t_2 - t_1)}{\hbar} \right) | q_1 x_1 \rangle &= \int_{q_1}^{q_2} Dq K[x_2, x_1; q(t)] \exp \left[ \frac{i}{\hbar} \int_{t_1}^{t_2} dt \frac{1}{2} \mu \right. \\
&\quad \left. \times (\dot{q}(t))^2 \right]
\end{aligned}
\tag{IIIa.3}$$

where  $K$  is the electronic propagator

$$K[x_2, x_1; q(t)] = \int_{x_1}^{x_2} Dx \exp \left[ \frac{i}{\hbar} \int_{t_1}^{t_2} dt \{ T_x - V(x, q(t)) \} \right] ,
\tag{IIIa.4}$$

which is a functional of the nuclear path, i.e., it depends on the particular choice of the nuclear trajectory  $q(t)$ .

The times  $t_1$  and  $t_2$  are usually taken to be the infinite past and infinite future respectively, when  $q_1, q_2 \rightarrow \infty$ , and the system is in asymptotic electronic state  $\phi_1(x_1)$  or  $\phi_2(x_2)$ , which are eigenfunctions of the Hamiltonian  $\lim_{q \rightarrow \infty} H_{el}(q, x)$ . Instead of

the propagator (IIIa.1), Pechukas noted that one actually requires the propagator in 'state' rather than coordinate representation:

$$\begin{aligned}
& \langle 2, q_2 | \exp[-iH(t_2 - t_1)/\hbar] | 1, q_1 \rangle \\
&= \int dx_2 \int dx_1 \langle 2 | x_2 \rangle \langle x_2, q_2 | \exp[-iH(t_2 - t_1)/\hbar] | q_1 x_1 \rangle \langle x_1 | 1 \rangle \\
&= \int dx_2 \int dx_1 \phi_2^*(x_2) \langle q_2 x_2 | \exp[-iH(t_2 - t_1)/\hbar] | q_1 x_1 \rangle \phi_1(x_1)
\end{aligned}
\tag{IIIa.5}$$

Using (IIIa.3), the 'state' representation propagator takes the form

$$\langle 2, q_2 | \exp\left\{\frac{-iH'(t_2 - t_1)}{\hbar}\right\} | 1, q_1 \rangle = \int_{q_1}^{q_2} Dq \, K_{21}[q(t)] \exp\left[\frac{i}{\hbar} \int_{t_1}^{t_2} dt \left( \frac{1}{2} \mu \dot{q}(t)^2 \right)\right] \quad (\text{IIIa.6})$$

where

$$K_{21}[q(t)] = \int dx_1 \int dx_2 \phi_2^*(x_2) \int_{x_1}^{x_2} Dx \exp\left[\frac{i}{\hbar} \int_{t_1}^{t_2} dt \{T_x - V(q(t), x)\}\right] \phi_1(x_1) \quad (\text{IIIa.7})$$

is the electronic transition amplitude. It gives the transition amplitude (1→2 electronic transition) with the nuclei constrained to follow the trajectory  $q(t)$ . S-matrix elements for the  $1n_1 \rightarrow 2n_2$  transition, where  $n_1$  and  $n_2$  are the initial and final values of the quantum numbers for the nuclear degrees of freedom, are then constructed in a way analogous to the development following (Id.11).

Retracing our steps slightly, we see that the calculation of  $K_{21}[q(t)]$ , which is the determination of the electronic transition amplitude under a fixed nuclear trajectory, is none other than what we set out to do via the semiclassical time-dependent formalism in Section II.  $K_{21}$  is none other than

$$a_2 \exp\left\{\frac{-i}{\hbar} \int_{t_1}^{t_2} dt U_{22}^a(q(t))\right\} \quad [\text{see (II.6)}]; \text{ and } q(t) \text{ was chosen to be}$$

the straightline trajectory for both the Landau-Zener and the Demkov models. In the next subsection we will present a semiclassical form for  $K[q(t)]$  which is valid for all classical paths. This result is then used in (IIIa.6), in which the path integral over  $q$  is done using the stationary phase approximation, which effectively selects out the classical paths, out of infinitely many possible ones. Then everything follows exactly as the development subsequent to (Id.11).

### IIIb. The Electronic Propagator and Analytic Continuation of Classical Mechanics

As already remarked the determination of the electronic propagators  $K_{21}$  (or  $K_{11}$ ) is equivalent to the solution of (II.9). The  $K$ 's are given in terms of the  $a$ 's by:

$$K_{21}[q(t)] = a_2(t_2) \exp\left[\frac{-i}{\hbar} \int_{t_1}^{t_2} dt W_2(t)\right] \quad (\text{IIIb.1a})$$

$$K_{11}[q(t)] = a_1(t_1) \exp\left[\frac{-i}{\hbar} \int_{t_1}^{t_2} dt W_1(t)\right] \quad (\text{IIIb.1b})$$

where the  $W$ 's are the adiabatic potential energy surfaces.

We will briefly indicate the semiclassical solution for the two-state case as provided by Miller and George via the first order perturbation solution for  $a_2$  (with the initial conditions  $a_1(t_1)=1$ ,  $a_2(t_1)=0$ ). (III.9) gives

$$a_2(t_2) = -\frac{i}{\hbar} \int_{t_1}^{t_2} dt C_{21} \exp\left\{\frac{i}{\hbar} \int_{t_1}^t dt' (W_2 - W_1)\right\} . \quad (\text{IIIb.2})$$

Hence, from (IIIb.1a)

$$\begin{aligned} K_{21}[q(t)] &= -\frac{i}{\hbar} \int_{t_1}^{t_2} dt C_{21} \exp\left\{\frac{i}{\hbar} \int_{t_1}^t dt' (W_2 - W_1)\right\} \exp\left\{-\frac{i}{\hbar} \int_{t_1}^{t_2} dt' W_2\right\} \\ &= -\frac{i}{\hbar} \int_{t_1}^{t_2} dt C_{21} \exp\left\{-\frac{i}{\hbar} \int_{t_1}^t dt' W_1(t') - \frac{i}{\hbar} \int_t^{t_2} dt' W_2(t')\right\} , \end{aligned} \quad (\text{IIIb.3})$$

which can conveniently be interpreted as an integral over  $t$  of transition amplitudes for transitions from  $W_1$  to  $W_2$  at particular times  $t$ . One now proceeds to the classical limit by attempting to do the integral using the stationary phase approximation, i.e., one requires that

$$\frac{d}{dt} \left( \int_{t_1}^t dt' W_1(t') + \int_t^{t_2} dt' W_2(t') \right) = 0$$

$$\text{or} \quad W_1(t) - W_2(t) = 0 . \quad (\text{IIIb.4})$$

The solution of (IIIb.4) is in general complex, which means in (IIIb.3) one needs to evaluate the nonadiabatic coupling  $C_{12}$  for a complex time. In order to avoid this, one applies the stationary phase approximation to the next order of accuracy by looking for a time at which the phase of the integrand in (IIIb.3) is least rapidly varying, i.e.,

$$\frac{d^2}{dt^2} \left( \int_{t_1}^t dt' W_1(t') + \int_t^{t_2} dt' W_2(t') \right) = 0$$

$$\text{or} \quad \frac{d}{dt} (W_1(t) - W_2(t)) = -\frac{d}{dt} (\Delta W) = 0 \quad (\text{IIIb.5})$$

$$\text{where} \quad \Delta W = W_2 - W_1 .$$



Expanding the phase in a Taylor series about  $t_0$ , a solution to (IIIb.5), one has

$$\int_{t_1}^t dt' W_1(t') + \int_{t_0}^{t_2} dt' W_2(t') = \tau - (t-t_0) \Delta W_0 + 0 - \frac{1}{6}(t-t_0)^3 \times (\Delta W)_0'' + \dots \quad (\text{IIIb.6})$$

where

$$\tau = \int_{t_1}^{t_0} dt W_1(t) + \int_{t_0}^{t_2} dt W_2(t) ,$$

$$\Delta W_0 = \Delta W(t=t_0) ,$$

$$(\Delta W)_0'' = (d^2(\Delta W)/dt^2)_{t=t_0} .$$

(IIIb.3) becomes

$$K_{21}[q(t)] \approx -\frac{i}{\hbar} (C_{21})_{t_0} \exp\left(\frac{-i\tau}{\hbar}\right) \int_{-\infty}^{\infty} dt \exp\left(\frac{i}{\hbar} \Delta W_0(t-t_0) + \frac{i}{6\hbar} (\Delta W)_0''(t-t_0)^3\right) \quad (\text{IIIb.7})$$

where the integration limits have been extended to  $\pm\infty$ . The integral in (IIIb.5) is recognized as the integral representation of the Airy function, and invoking its asymptotic form gives

$$K_{21}[q(t)] \approx -\langle \phi_1 | \frac{\partial}{\partial t} \phi_2 \rangle_{t_0} \left[ \frac{2\pi\hbar}{(2\Delta W_0/(\Delta W)_0'')^{1/2}} \right]^{1/2} \times \exp\left[ -\frac{2}{3} \frac{\Delta W_0}{\hbar} \left( \frac{2\Delta W_0}{(\Delta W)_0''} \right)^{1/2} - \frac{i}{\hbar} \int_{t_1}^{t_0} dt W_1(t) - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t) \right] . \quad (\text{IIIb.8})$$

This approximate solution is recognized to resemble the exact Stuckelberg solution (WKB phase integral solution) for (II.9) most closely if the pre-exponential factor is set equal to 1. We thus write .

$$K_{21}[q(t)] = e^{-\delta} \exp\left[ -\frac{i}{\hbar} \int_{t_1}^{t_0} dt W_1(t) - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t) \right] \quad (\text{IIIb.9})$$

where

$$\delta = \frac{2}{3} \frac{\Delta W_0}{\hbar} \left( \frac{2\Delta W_0}{(\Delta W)_0''} \right)^{1/2}, \quad (\text{IIIb.10})$$

but whose general form is as yet undetermined. This general form can be obtained as follows. We already remarked that (IIIb.4) may not have real solutions, but it will always have complex solutions. For the avoided curve crossing case where  $t_0$  is the solution to (IIIb.5), we may expand  $\Delta W$  about  $t_0$  to obtain an approximate solution for (IIIb.4):

$$\Delta W(t) \approx \Delta W_0 + 0 + \frac{1}{2}(t-t_0)^2 (\Delta W)_0'' . \quad (\text{IIIb.11})$$

Hence  $t_*$ , a solution to  $\Delta W=0$ , is given to the above approximation by

$$t_* = t_0 + i \left( \frac{2\Delta W_0}{(\Delta W)_0''} \right)^{1/2}; \quad (\text{IIIb.12})$$

and it is immediately seen that  $t_*^*$  is also a solution. One then obtains

$$\begin{aligned} \int_{t_*^*}^{t_*} dt \Delta W(t) &= \int_{t_*^*}^{t_*} dt \left[ \Delta W_0 + \frac{1}{2}(t-t_0)^2 (\Delta W)_0'' \right] \\ &= i \frac{4}{3} \Delta W_0 \left( \frac{2\Delta W_0}{(\Delta W)_0''} \right)^{1/2} \\ &= 2 \int_{t_0}^{t_*} dt \Delta W(t) . \end{aligned} \quad (\text{IIIb.13})$$

Comparing with (IIIb.10) we see that

$$\delta = -\frac{i}{\hbar} \int_{t_0}^{t_*} dt \Delta W(t) , \quad (\text{IIIb.14})$$

which is the sought for general form, independent of the approximation introduced for  $\Delta W(t)$ . (IIIb.9) can then be written as

$$\begin{aligned} K_{21}[q(t)] &= \exp \left[ -\frac{i}{\hbar} \int_{t_1}^{t_0} dt W_1(t) - \frac{i}{\hbar} \int_{t_0}^{t_*} dt W_1(t) - \frac{i}{\hbar} \int_{t_*}^{t_0} dt W_2(t) \right. \\ &\quad \left. - \frac{i}{\hbar} \int_{t_0}^{t_2} dt W_2(t) \right] \end{aligned}$$

$$= \exp \left[ -\frac{i}{\hbar} \int_{t_1}^{t_*} dt W_1[q(t)] - \frac{i}{\hbar} \int_{t_*}^{t_2} dt W_2[q(t)] \right] . \quad (\text{IIIb.15})$$

This last equation gives the general semiclassical solution for the electronic propagator.

With (IIIb.15), the propagator for nonadiabatic transition (IIIa.6) becomes

$$\begin{aligned} \langle 2, q_2 | \exp \left( \frac{-iH(t_2 - t_1)}{\hbar} \right) | 1, q_1 \rangle \\ = \int_{q_1}^{q_2} Dq \exp \left[ \frac{i}{\hbar} \int_{t_1}^{t_2} dt \frac{1}{2} \mu (\dot{q}(t))^2 - \frac{i}{\hbar} \int_{t_1}^{t_*} dt W_1(q(t)) - \frac{i}{\hbar} \int_{t_*}^{t_2} dt W_2(q(t)) \right]. \end{aligned} \quad (\text{IIIb.16})$$

It is instructive to compare this equation with the expression for the electronically adiabatic propagator

$$\begin{aligned} \langle q_2 | \exp \left( \frac{-iH(t_2 - t_1)}{\hbar} \right) | q_1 \rangle = \int_{q_1}^{q_2} Dq \exp \left[ \frac{i}{\hbar} \int_{t_1}^{t_2} dt \frac{1}{2} \mu (\dot{q}(t))^2 \right. \\ \left. - \frac{i}{\hbar} \int_{t_1}^{t_2} dt V(q(t)) \right] , \end{aligned} \quad (\text{IIIb.17})$$

where  $V(q)$  is the single potential surface for the adiabatic motion. (IIIb.16) has the following physical interpretation. Instead of moving on the single surface  $V(q)$ , the nuclei make the nonadiabatic transition at the complex time  $t_*$  from one adiabatic surface to another ( $W_1 \rightarrow W_2$ ). Since  $t_*$  is complex, nonadiabatic transitions are in general classically forbidden processes, and the interesting conclusion emerges that classically forbidden processes can be described by the analytic continuation of classical mechanics into the complex time (or coordinate) domain.

As mentioned earlier, the nuclear path integral in (IIIb.16) (which, like its electronic counterpart, is never evaluated in practice) is carried out again by the stationary phase approximation to give:

$$\langle 2q_2 | \exp \left( \frac{-iH(t_2 - t_1)}{\hbar} \right) | 1q_1 \rangle = \left[ (-2\pi i \hbar)^N \left( \frac{\partial q_2}{\partial p_1} \right)_{q_1} \right]^{-1/2} \exp \left[ \frac{i\phi_{2,1}(q_2, q_1)}{\hbar} \right] , \quad (\text{IIIb.18})$$

where  $N$  is the number of nuclear degrees of freedom,  $p_1$ , is the momentum conjugate to  $q_1$ , and  $\phi_{2,1}$  is the action integral

$$\phi_{2,1}(q_2, q_1) = \int_{t_1}^{t_2} dt \frac{1}{2} \mu \dot{q}(t)^2 - \int_{t_1}^{t_*} dt W_1 - \int_{t_*}^{t_2} dt W_2 \quad (\text{IIIb.19})$$

This integral is evaluated along the classical trajectory (obtained by integrating Hamilton's equations) which is determined by double-ended boundary conditions  $q_1$  and  $q_2$  and which change from potential  $W_1$  to  $W_2$  at complex time  $t_*$ .

Analogous to (Id.33), the expression for the nonadiabatic transition S-matrix element can be written

$$S_{2n_2, 1n_1} = i \left[ (-2\pi i \hbar)^{N-1} \left( \frac{\partial n_2}{\partial q_1'} \right)_{n_1} \right]^{-1/2} \times \exp \left[ -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt \{ \rho(t) \dot{P}(t) + q(t) \dot{n}(t) \} \right] \quad (\text{IIIb.20})$$

where  $\rho, P$  are the nuclear translational and  $q, n$  the nuclear internal degrees of freedom. (Note that in previous equations of this section  $q$  stands for the totality of nuclear degrees of freedom). In the evaluation of the integral in (IIIb.20), the complex trajectories will yield exponential damping factors characteristic of classically forbidden processes.

Finally we point out that in the case of one-dimensional nuclear motion (atom-atom collisions), (IIIb.20) reduces to the Stueckelberg solution given by (IIc.9) to (IIc.13), with  $\xi = \pi/4$ .

### IIIc. Examples of Nonadiabatic Transition Probabilities in the Miller-George Theory

We will consider the Landau-Zener and the Demkov models in this subsection. The Landau-Zener model is given, in the diabatic representation by (IIa.1) and (IIa.2). In the adiabatic representation the potential surfaces  $W_i$  are given by (IIa.4), (here  $W_i$  stands for  $U_{ii}^a$ ). To calculate the local transition probability  $e^{-2\delta}$  [see (IIIb.7)], we need  $\delta$  as given by (IIIb.12). This can be changed into an integral over  $R$ , the translational nuclear coordinate, if we assume the straight-line trajectory (IIa.3). We have, for a 'once passage' through the nonadiabatic coupling region:

$$P_{2,1} = |S_{2 \rightarrow 1}|^2 = \exp(-2\delta) \quad (\text{IIIc.1})$$

where

$$\delta = - \frac{i}{2\hbar} \int_{t_*}^{t_*} dt \Delta W(t)$$

$$= - \frac{i}{2\hbar v_0} \int_{R_*}^{R_*} dR \Delta W(R) \quad , \quad (\text{IIIc.2})$$

and  $R_* = R(t=t_*)$  is the complex coordinate at which  $\Delta W=0$ . From (IIa.4),

$$\Delta W = [(\Delta F)^2 (R-R_0)^2 + 4a^2]^{1/2} \quad . \quad (\text{IIIc.3})$$

Hence

$$R_* = R_0 + 2i a/(\Delta F) \quad . \quad (\text{IIIc.4})$$

To do the integral in (IIIc.2) it is convenient to change the variable of integration to  $x$ , where

$$R = R_0 + 2i x a/(\Delta F) \quad .$$

(IIIc.2) then becomes

$$\delta = \frac{2a^2}{\hbar v_0 \Delta F} \int_{-1}^1 dx \sqrt{1-x^2} \quad . \quad (\text{IIIc.5})$$

Elementary integration yields

$$\delta = \frac{\pi a^2}{\hbar v_0 \Delta F} \quad . \quad (\text{IIIc.6})$$

Finally

$$P_{2,1} = \exp(-2\delta) = \exp\left[\frac{-2\pi a^2}{\hbar v_0 \Delta F}\right] \quad (\text{IIIc.7})$$

which is the same result as obtained in (IIa.8).

We now consider the Demkov model given in the adiabatic representation by (IIb.3), which gives

$$\Delta W = [\Delta^2 + 4A^2 \exp(-2\lambda R)]^{1/2} \quad . \quad (\text{IIIc.8})$$

The solution to  $\Delta W=0$  gives a sequence a complex roots

$$R_* = - \frac{1}{\lambda} \ln\left(\frac{\Delta}{2A}\right) + \frac{i\pi}{2\lambda} (2n+1), \quad n=0,1,2,\dots \quad (\text{IIIc.9})$$

To do the integral (IIIc.2), we use the principle root, i.e., the one which is closest to the real axis and leads to the largest  $P_{2,1}$ . We pick

$$R_* = -\frac{1}{\lambda} \ln\left(\frac{\Delta}{2A}\right) + \frac{i\pi}{2\lambda} . \quad (\text{IIIc.10})$$

Effecting the change of variables  $R \rightarrow x$ , where

$$R = -\frac{1}{\lambda} \ln\left(\frac{\Delta}{2A}\right) + \frac{i\pi x}{2\lambda} , \quad (\text{IIIc.11})$$

the R-integral in (IIIc.2) becomes

$$\delta = \frac{\pi\Delta}{2\lambda\hbar v_0} \int_{-1}^1 dx (1+e^{-i\pi x})^{1/2} . \quad (\text{IIIc.12})$$

This gives

$$\delta = \frac{\pi\Delta}{2\lambda\hbar v_0}$$

and

$$P_{21} = \exp[-\pi\Delta/(\lambda\hbar v_0)] . \quad (\text{IIIc.13})$$

For large  $\delta$ , this is essentially the same result as obtained in (IIb.7).

#### IIId. Analytic Structure of Adiabatic Potential Surfaces

The most appealing nature of the Miller-George theory lies in its description of nonadiabatic transitions: a non-adiabatic transition can be described by a classical trajectory moving continuously from one adiabatic surface to another, which become degenerate at some complex time (coordinate) point. In fact the two surfaces can be pictured as two pieces of the same surface, so that what appears to be a transition in real time (or coordinate) space is really no transition at all when the trajectory is allowed to be complex. The dynamical information embedded in the nonadiabatic couplings, which are not required in the present formalism at all, is completely contained in the analytic structure of the adiabatic potential surface, i.e., when  $W_1$  is regarded as a complex function of either  $R$  or  $t$ . This is indeed an intellectually pleasing and physically cogent way to look at nonadiabatic transitions.

The theory of analytic functions provides the natural framework for the description of the adiabatic potential surfaces. For the two state case

$$W_{1,2} = \frac{U_{11}^d + U_{22}^d}{2} \mp \frac{1}{2} [(U_{22}^d - U_{11}^d)^2 + 4(U_{12}^d)^2]^{1/2} . \quad (\text{IIId.1})$$

The surfaces  $W_{1,2}$  are the roots of the quadratic equation

$$(U_{11}^d - W)(U_{22}^d - W) - (U_{12}^d)^2 = 0 , \quad (\text{IIIId.2})$$

and as such are the two branches of the same analytic function  $W(R)$ , with the branch point at  $R_*$  where

$$\Delta W(R_*) = [(U_{22}^d - U_{11}^d)^2 + 4(U_{12}^d)^2] = 0 \quad (\text{IIIId.3})$$

$W_1$  and  $W_2$  are also known as the two Riemann sheets of the same analytic function  $W(R)$ , which is double-valued.  $W$  can, of course, also be considered as a function of  $t$ . Let the complex variable  $z$  be either  $R$  or  $t$ . Starting from an arbitrary point  $z_0$  and following any contour which winds around  $z_*$  (the branch point) once and ends up back on  $z_0$ , or traverses a branch cut (emanating from  $z_0$ ) once, one would go from one Riemann sheet of  $W$  to the next. Any contour, however, which does not encircle any branch point or which does not traverse any branch cut will force  $W(z)$  to stay on the sheet it begins with. It is at the point where the contour traverses the branch cut that  $W_1$  goes over to  $W_2$  or vice versa. Consider the first equality in (IIIb.15). The sum of integrals can be written as one complex integral

$$\int_{C(t_1 \rightarrow t_2)} dt W(t) , \quad (\text{IIIId.4})$$

where the contour, from  $t_1$  to  $t_2$ , is represented in Figure 2 (solid line). Because of the analytic nature of  $W$ , the contour does not have to go exactly through  $t_*$ . In fact, any distorted contour from  $t_1$  to  $t_2$  traversing the cut at some point will suffice (such as the dashed contour in Figure 2).

In much the same way we can discuss nonadiabatic transitions in multistate problems. Analogous to (IIIId.2) the  $N$  adiabatic surfaces of an  $N$ -state problem are obtained by the solution of the secular equation

$$\det[\underline{U}^d - W\underline{1}] = 0 . \quad (\text{IIIId.5})$$

The  $N \times N$  determinant leads to an  $N$ th-order polynomial in  $W$ . The  $N$  different roots of this polynomial are essentially the  $N$  different branches, or Riemann sheets, of the  $N$ th root analytic function  $W$ . As in the 2-state case, trajectories that make transitions from one branch to another can be really considered to be propagated on a single surface, although they would be required to go around appropriate branch points.

For a transition from state  $\alpha$  to  $\beta$  in an  $N$ -state problem, the nuclear path integral can in general be written [compare with (IIIb.18) and (IIIb.19)]:

$$\begin{aligned} \langle \beta q_2 | \exp \left( \frac{-iH(t_2 - t_1)}{\hbar} \right) | \alpha q_1 \rangle &= \left[ (-2\pi i \hbar)^M \left( \frac{\partial q_2}{\partial p_1} \right)_{q_1} \right]^{-1/2} \\ &\times \exp \left\{ \frac{i}{\hbar} \int_{C_{\beta\alpha}(t_1 \rightarrow t_2)} dt \left[ \frac{1}{2} \mu (\dot{q}(t))^2 - W(q(t)) \right] \right\} \quad (\text{IIIId.6}) \end{aligned}$$

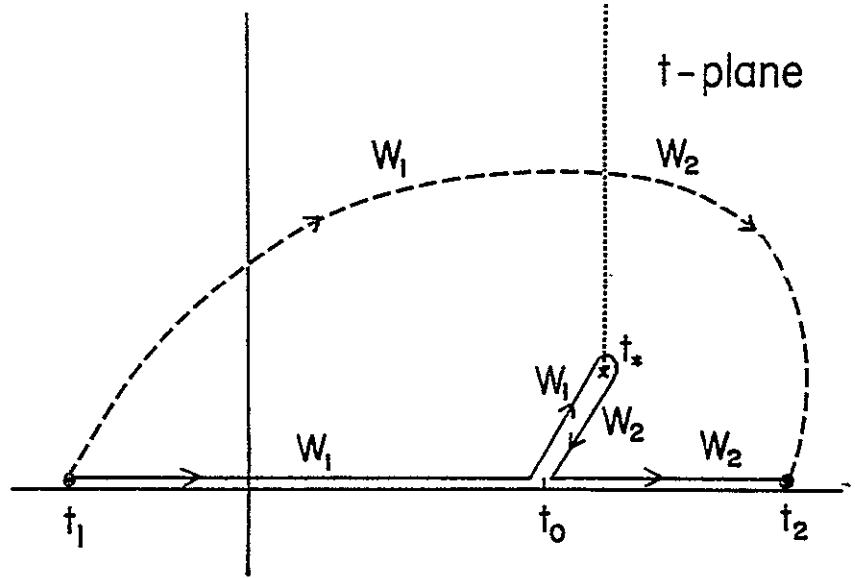


Fig. 2. Contour of integration (—) for the electronic propagator in (IIIb.15). In general  $t_0 \sim \text{Re}(t_*)$ . The displacement is accentuated here for clarity. The dotted line represents the branch cut. The distorted contour (dashed) is also acceptable for the calculation of the electronic propagator. The  $W$ 's represent the sheets used for various parts of the contours.



where  $M$  is the number of nuclear degrees of freedom. In (IIIId.6)  $W$  is the  $N$ -valued analytic adiabatic surface.  $C_{\beta\alpha}$  is a contour in the complex time plane connecting  $t_1$  and  $t_2$  and winds around the appropriate branch points of  $W$  in such a way that the trajectory beginning on Riemann sheet  $\alpha$  (the  $\alpha$  electronic state) at  $t_1$  finishes up on Riemann sheet  $\beta$  (the  $\beta$  electronic state) at  $t_2$ .  $q(t)$  is the classical trajectory obtained by integrating Hamilton's equations along the complex contour  $C_{\beta\alpha}(t_1 \rightarrow t_2)$ .

Before leaving our discussion of the analytic structure of adiabatic potential surfaces, we would like to mention a practical problem connected with the calculation of  $\delta$  in (IIIb.12). In most cases other than the Landau-Zener model of straight-line potentials (for instance, the Demkov model), there will be more than one branch point for  $W(t)$ . For large  $\delta$ , that is, small transition probability, it will be usually sufficient to take the branch point closest to the real axis and compute  $\delta$  as though there were only one branch point (as we did for the Demkov model). For small  $\delta$ , however, this procedure may not always be sufficient. For this case, the formula for the local transition probability

$$p \approx \exp(-2\delta_0) ,$$

where  $\delta_0$  is computed using the branch point closest to the real axis, may require some correction.

The correction procedure usually employed is to replace  $\exp(-2\delta_0)$  by an expression which is the exact solution of a two-state exponential model due to Nikitin. The model is defined by

$$U_{11}^d = B \exp(-\beta R) + \frac{\Delta\epsilon}{2} - \frac{A}{2} \cos\theta \exp(-\beta R) \quad (\text{IIIId.7a})$$

$$U_{22}^d = B \exp(-\beta R) - \frac{\Delta\epsilon}{2} + \frac{A}{2} \cos\theta \exp(-\beta R) \quad (\text{IIIId.7b})$$

$$U_{12}^d = U_{21}^d = -\frac{A}{2} \sin\theta \exp(-\beta R) \quad (\text{IIIId.7c})$$

where  $\Delta\epsilon, \beta, A, B$  and  $\theta$  are all constants.  $\underline{U}^d$  can be diagonalized to obtain the adiabatic potentials

$$W_{1,2} = B \exp(-\beta R) \mp \frac{\Delta\epsilon}{2} [1 - 2\cos\theta \exp(-\beta(R-R_p)) + \exp(-2\beta(R-R_p))]^{1/2} \quad (\text{IIIId.8})$$

where  $R_p$  is the 'center' of the nonadiabaticity region defined by

$$\exp(-\beta R_p) = \Delta\epsilon . \quad (\text{IIIId.9})$$

In this model  $\Delta\epsilon$  is the asymptotic splitting of  $W_1$  and  $W_2$ , and  $1/\beta$  is the characteristic length of the nonadiabatic coupling. If the matrix that diagonalizes  $\underline{U}^d$  is written as in (Ib.25),

(Ib.26) implies that

$$2\alpha = \tan^{-1} \left( \frac{-A \sin\theta \exp(-\beta R)}{\Delta\epsilon - A \cos\theta \exp(-\beta R)} \right) . \quad (\text{IIIId.10})$$

Hence  $\alpha \rightarrow 0$  at  $R \rightarrow \infty$  ; (IIIId.11)

and  $2\alpha \rightarrow \theta$  at  $R \ll R_p$  . (IIIId.12)

Assuming a straight line-trajectory  $\Delta R = v_0 t$ , the exact solution of (II.9) or (IIb.5) gives the Nikitin result for  $p$ , which incorporates the effect of the multiplicity of branch points:

$$p = \exp \left[ -\frac{\pi}{4} \delta_0 (1 - \cos\theta) \right] \left[ \frac{\sinh [ (\pi/4) \delta_0 (1 + \cos\theta) ]}{\sinh (\pi \delta_0 / 2)} \right] . \quad (\text{IIIId.13})$$

This is the correction formula (sometimes known as the Nikitin formula) used in most applications with exponential-like diabatic curves.  $\delta_0$  is calculated by using (IIIb.12), with  $t_*$  being the branch point of  $W(t)$  closest to the real axis.  $\theta$  is obtained from (IIIId.12).

#### IV. APPLICATIONS OF THE SEMICLASSICAL S-MATRIX

We will discuss two classes of problems, electronically adiabatic and electronically nonadiabatic problems. The former makes use of the formalism presented in Section Id, and provides the perspective and motivation for its generalization to the latter, which relies on Section III.

##### IVa. Electronically Adiabatic Collisions

The example we will discuss is vibrational excitation in collinear  $A+BC$ , both classically allowed and classically forbidden. Since electronic degrees of freedom are not explicitly considered, all dynamics is treated classically. The system has only two degrees of freedom, one translational  $R$ , and one vibrational (internal)  $r$ . The completely classical Hamiltonian can be written as

$$H(P, R, p, r) = \frac{P^2}{2\mu} + \frac{p^2}{2m} + v(r) + V(R, r) , \quad (\text{IVa.1})$$

where  $\mu$  and  $m$  are the reduced masses for the two degrees of freedom,  $v(r)$  is the vibrational potential for  $BC$ , and  $V(R, r)$  is the interaction potential coupling translation and vibration.

Following (Id.12) we have to assign  $(n, q)$ , the action-angle variables suitable for this problem. The action variable

$n$  is the classical counterpart of the vibrational quantum number for the free BC. The WKB quantum conditions require that

$$(n + \frac{1}{2})\pi = \frac{(2m)^{1/2}}{\hbar} \int_{r_<}^{r_>} dr [\varepsilon - v(r)]^{1/2} \quad (\text{IVa.2})$$

where 
$$\varepsilon = \frac{p^2}{2m} + v(r) \quad (\text{IVa.3})$$

and  $r_<, r_>$  are the classical turning points. The angle variable  $q$  is given by

$$q = \frac{(2m/\hbar^2)^{1/2}}{n'(\varepsilon)} \int_{r_<}^r dr' [\varepsilon - v(r')]^{1/2}, \quad (\text{IVa.4})$$

where  $n(\varepsilon)$  is the function defined by (IVa.2). The Hamiltonian (Id.12) becomes

$$H(P, R, n, q) = \frac{p^2}{2\mu} + \varepsilon(n) + V(r(n, q), R) \quad (\text{IVa.5})$$

$$\equiv H_0 + V$$

where  $\varepsilon(n)$  is the inverse function of  $n(\varepsilon)$ . For a simple harmonic oscillator

$$v(r) = \frac{1}{2} m\omega^2 (r - r_0)^2. \quad (\text{IVa.6})$$

Using (IVa.2) and (IVa.4), one obtains

$$\varepsilon(n) = (n + \frac{1}{2})\hbar\omega \quad (\text{IVa.7})$$

and 
$$r(n, q) = r_0 + \left( \frac{(2n+1)\hbar}{m\omega} \right)^{1/2} \sin q. \quad (\text{IVa.8})$$

For the general case one can expand the potential:

$$v(r) = \frac{1}{2} m\omega^2 (r-r_0)^2 [1 + a_1 (r-r_0)/r_0 + a_2 (r-r_0)^2/r_0^2 + \dots] , \quad (\text{IVa.9})$$

and  $\varepsilon(n)$  and  $r(n, q)$  can then be constructed as powers series in  $\lambda = (2m\omega r_0^2)^{-1}$ . For most diatomic  $\lambda \ll 1$  and it is usually sufficient to retain terms up to first or second order in  $\lambda$ .

For a transition between the vibrational states  $n_1$  and  $n_2$ , the S-matrix, following (Id.33), is given by

$$s_{\vec{n}_2, \vec{n}_1}(E) = i [ (-2\pi i \hbar) \left( \frac{\partial n_2}{\partial \bar{q}_1} \right)_{n_1} ]^{-1/2} \exp[i \frac{\Phi}{\hbar} (n_2, n_1)] , \quad (\text{IVa.10})$$

$$\text{where } \Phi(n_2, n_1) = - \int_{-\infty}^{\infty} dt [R(t) \dot{P}(t) - q(t) \dot{n}(t)] , \quad (\text{IVa.11})$$

and  $\bar{q}_1$  is the one-dimensional analog of  $\vec{q}_1$  in (Id.34). The classical trajectories  $q(t)$  and  $R(t)$  are determined by the integration of Hamilton's equations

$$\dot{q} = \partial H(P, R, n, q) / \partial n , \quad (\text{IVa.12a})$$

$$\dot{R} = \partial H(P, R, n, q) / \partial P , \quad (\text{IVa.12b})$$

$$\dot{n} = -\partial H(P, R, n, q) / \partial q ,$$

$$\dot{P} = -\partial H(P, R, n, q) / \partial R .$$

We must now specify the boundary conditions for this problem. First  $E$ , the total energy, is an input parameter, as are  $n_1$  and  $n_2$ , the initial and final vibrational quantum numbers, both required to be integers. The boundary conditions are then

$$n_1 = \text{specified integer} \quad (\text{IVa.13a})$$

$$n_2 = \text{specified integer} \quad (\text{IVa.13b})$$

$$P_1 = -\{2\mu[E - \epsilon(n_1)]\}^{1/2} \quad (\text{IVa.13c})$$

$$P_2 = +\{2\mu[E - \epsilon(n_2)]\}^{1/2} \quad (\text{IVa.13d})$$

Note that once  $n_1$  and  $n_2$  are fixed,  $P_1$  and  $P_2$  will also be fixed by (IVa.13c) and (IVa.13d). One thus starts a trajectory with the initial conditions

$$n_1 = \text{specified integer} \quad (\text{IVa.14a})$$

$$R_1 = \text{asymptotically large} \quad (\text{IVa.14b})$$

$$P_1 = -\{2\mu[E - \epsilon(n_1)]\}^{1/2} \quad (\text{IVa.14c})$$

$$q_1 = \bar{q}_1 + \epsilon'(n_1) \frac{\mu R_1}{P_1} \quad (\text{IVa.14d})$$

[which is actually the same set of equations as (Id.34)]. In (IVa.14d)  $\epsilon'(n_1)\mu R_1/P_1$  is fixed but  $\bar{q}_1$  is as yet unspecified. The idea is to choose representative values of  $\bar{q}_1$  in the range  $0 \leq \bar{q}_1 \leq 2\pi$ , and integrate Hamilton's equations (IVa.12) forward in

time until  $R_2[R(t=t_2)]$  is again asymptotically large and  $\dot{P}_2[(\dot{P}(t))_{t=t_2}] \rightarrow 0$ ; thus generating many trajectories with many final values for  $n_2$  (which may not be integral). In this way a functional relationship  $n_2(\bar{q}_1, n_1)$  is established. One then solves the equation

$$n_2(\bar{q}_1, n_1) = n_2 \quad (\text{IVa.15})$$

for  $\bar{q}_1$ , where  $n_2$  on the right is the specified final vibrational quantum number of the problem. Associated with each root of (IVa.15) for  $\bar{q}_1$  is an action integral  $\Phi$  and a pre-exponential derivative  $(\partial n_2 / \partial \bar{q}_1)_{n_1}$ ; and the S-matrix  $S_{n_2 n_1}$  is a sum of terms like (IVa.10), one for each root  $\bar{q}_1$ .

Since for any solution  $\bar{q}_1$  to (IVa.15)  $\bar{q}_1 + 2\pi$  is also a solution, there must be an even number of roots to (IVa.15). Moreover, since  $n_2(\bar{q}_1)$  is periodic with period  $2\pi$ , any two solutions  $\bar{q}_I$  and  $\bar{q}_{II}$  within an interval of  $2\pi$  must be such that  $(\partial n_2 / \partial \bar{q}_1)_{\bar{q}_I}$  and  $(\partial n_2 / \partial \bar{q}_1)_{\bar{q}_{II}}$  have opposite signs. We consider the case where there are two solutions  $q_I$  and  $q_{II}$  in the interval  $0 \leq q_1 \leq 2\pi$ . Let the two action integrals (IVa.11) associated with these two solutions be  $\Phi_I$  and  $\Phi_{II}$  respectively. Then the S-matrix is given by

$$S_{n_2 n_1} = [-2\pi i \hbar |n'_2(q_I)|]^{-1/2} \exp\left(\frac{i}{\hbar} \Phi_I\right) + [+2\pi i \hbar |n'_2(q_{II})|]^{-1/2} \times \exp\left(\frac{i}{\hbar} \Phi_{II}\right), \quad (\text{IVa.16})$$

where the  $i$  outside the pre-exponential factor in (IVa.10) has been suppressed because it does not affect the value of  $|S_{n_2 n_1}|^2$ . Keeping proper track of the signs and the  $i$ 's in (IVa.16), it can be rewritten as

$$S_{n_2 n_1} = p_I^{1/2} \exp\left(\frac{i\pi}{4} + \frac{i}{\hbar} \Phi_I\right) + p_{II}^{1/2} \exp\left(-\frac{i\pi}{4} + \frac{i}{\hbar} \Phi_{II}\right) \quad (\text{IVa.17})$$

$$\text{where} \quad p_I = [2\pi \hbar |n'_2(q_I)|]^{-1}, \quad (\text{IVa.18})$$

$$p_{II} = [2\pi \hbar |n'_2(q_{II})|]^{-1} \quad (\text{IVa.19})$$

are the pre-exponential probability factors. (IVa.17) clearly reveals the quantum superposition effect inherent in the semi-classical formulation. The transition probability is

$$P_{n_2 n_1} = |S_{n_2 n_1}|^2 = p_I + p_{II} + 2(p_I p_{II})^{1/2} \sin(\Phi_{II} - \Phi_I). \quad (\text{IVa.20})$$

It is worthwhile to note here that the oscillatory result in (IVa.20) is also characteristic of the nonadiabatic Stuckelberg

type transitions discussed in the next subsection (Stuckelberg oscillations), both being the result of quantum superposition. The completely classical result, which adds probabilities instead of probability amplitudes, is

$$P_{n_2 n_1}^{CL} = P_I + P_{II} . \quad (IVa.21)$$

So far we have only described the situation when there are real solutions to (IVa.15), i.e., when the transition is classically allowed. However, transitions may be classically forbidden in the sense that no real solutions exist for (IVa.15) even though the state  $n_2$  is energetically accessible [ $E > \epsilon(n_2)$ ]. In such cases one is forced to consider the complex roots of (IVa.15). To see this explicitly one may expand  $n_2(q_1)$  about  $q_{\max}$ , the real value of  $q_1$  that would lead to the maximum real value of  $n_2$ , which we denote  $n_2^{\max}$ :

$$n_2(\bar{q}_1) = n_2^{\max} + \frac{1}{2} n_2''(\bar{q}_{\max}) (\bar{q}_1 - \bar{q}_{\max})^2 + \dots \quad (IVa.23)$$

Suppose the designated  $n_2$  is larger than  $n_2^{\max}$ , so that there are no real solutions to (IVa.15). Complex solutions, however, exist, and are approximately given by

$$\bar{q}_1 \approx \bar{q}_{\max} \pm i \left[ \frac{2(n_2 - n_2^{\max})}{|n_2''(\bar{q}_{\max})|} \right]^{1/2} . \quad (IVa.24)$$

The set of initial conditions (IVa.14), with complex  $\bar{q}_1$ , is of course still good for the integration of Hamilton's equations (IVa.12). All that is physically required is that  $n_1, P_1, R_1, n_2, R_2, P_2$  are all real at asymptotic regions.  $q_2$  is not physically observable and can acquire any real or complex value. That the initial variables  $n_1, P_1, R_1$  are all real is specified by the problem.  $n_2$  is required to be real, which automatically implies that  $P_2$  is also real [(IVa.13d)].  $R_2$ , however, will in general be complex for large real  $t$  if  $\bar{q}_1$  is complex, since the Hamiltonian (IVa.5) couples all the variables during the propagation of a trajectory.

Hence we seem to be running into a dilemma with the possible complexity of  $R_2$ . But the difficulty only arises if we require  $t_2$  to be real. If  $t_2$  can be made complex in an appropriate way,  $R_2$  can be made real. Actually the constraint of real  $t_2$  need not be applied on any physical grounds: since in this formulation,  $E$  has been made exact, and by the uncertainty principle its conjugate variable,  $t$ , can be anything, and thus possibly complex.

Suppose at an asymptotic real time  $\tilde{t}_2$ ,  $n(t) = n_2$  and  $P(t) = P_2$ . Propagating further in time will not change either  $n(t)$  or  $P(t)$ . However, Hamilton's equations imply that

$$R(t) = R(\tilde{t}_2) + \frac{P_2}{\mu}(t - \tilde{t}_2) . \quad (\text{IVa.25})$$

Now  $R(\tilde{t}_2)$  may in general be complex, but  $R(t_2)$  can be made real if the final time  $t_2$  is chosen to be

$$t_2 = \tilde{t}_2 - i \frac{\mu}{P_2} \text{Im}R(\tilde{t}_2) . \quad (\text{IVa.26})$$

This explicitly shows that in order to have final dynamical variables all real, the final time  $t_2$  may have to be complex when classically forbidden processes are considered.

If  $q_I$  is a complex root of (IVa.15), it is seen from (IVa.24) that the other root is  $q_I^*$ . Hence, as in the classically allowed case, it appears that there will also be two terms in the S-matrix. Now both  $\phi_I$  and  $\phi_{II}$  will be complex; but it can be shown that if  $\bar{q}_I$  is the root leading to an exponentially damping term  $\exp[-\text{Im}\phi_I]$ , the other root will lead to an exponentially growing term  $\exp[+\text{Im}\phi_I]$ . Thus in the S-matrix, only one term should be retained, the one leading to damping:

$$S_{n_2, n_1} = [-2\pi i \hbar n_2'(q_I)]^{-1/2} \exp(i\phi_I/\hbar) \quad (\text{IVa.27})$$

and the transition probability is

$$P_{n_2, n_1} = [2\pi \hbar |n_2'(q_I)|]^{-1} \exp\left(\frac{-2|\text{Im}\phi_I|}{\hbar}\right) \quad (\text{IVa.28})$$

which is reminiscent of the WKB result for tunnelling in one-dimensional systems.

(IVa.17) and (IVa.27) are called 'primitive' semiclassical results because they only work well for  $n_2 < n_2^{\text{max}}$  and  $n_2 > n_2^{\text{max}}$  independently, i.e., the separate solutions cannot be connected smoothly as  $n_2$  traverses  $n_2^{\text{max}}$ . In particular, when  $n_2$  approaches  $n_2^{\text{max}}$  arbitrarily closely, both (IVa.17) and (IVa.27) break down since  $|n_2'(q_{I, II})|^{-1} \rightarrow \infty$ . This situation recalls the classical rainbow effect. To remedy it, one has to introduce uniform semiclassical formulas which, in addition to effecting a smooth connection between  $n_2 < n_2^{\text{max}}$  and  $n_2 > n_2^{\text{max}}$ , will also approach the 'primitive' semiclassical results in regions where they work well.

#### IVb. Electronically Nonadiabatic Collisions

We consider here the collinear A+BC nonreactive collision process again, but with electronic transitions. A typical process of this type can be written

$$X(^2P_{1/2}) + H_2(n_1) \rightarrow X(^2P_{3/2}) + H_2(n_2) \quad (IVb.1)$$

where  $n_1(n_2)$  is the initial (final) vibrational quantum number of  $H_2$ , and the halogen  $X$  undergoes a spin-orbit electronic transition. The total Hamiltonian for this system can be written

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\eta} \frac{\partial^2}{\partial r^2} + H_{el} \quad (IVb.2)$$

where  $R$  is the translational  $X-H_2$  coordinate and  $r$  is the vibrational  $H_2$  coordinate.  $\mu$  and  $\eta$  are the reduced masses pertaining to  $R$  and  $r$  respectively.

In the previous subsection, both  $R$  and  $r$  are treated classically; and the nuclei are considered to be moving on a single electronic potential surface  $v(r)+V(R,r)$  [see (IVa.1)]. The transformation  $(p,r) \rightarrow (n,q)$  is then made, with the action-angle variables  $(n,q)$  still treated classically. Since an electronic transition is involved here, we have to consider at least two electronic surfaces (we will limit ourselves to exactly two). There are two equivalent ways to proceed using the Miller-George theory. One is using the electronic representation, i.e., finding an electronic basis set  $\phi(R,r,\vec{x})$  (where  $\vec{x}$  stands for electronic coordinates) which will generate the potential surfaces and couplings  $U_{ij}^d = \langle \phi_i | H_{el} | \phi_j \rangle_{\vec{x}}$  (the subscript

$\vec{x}$  means that brackets denote integration over electronic coordinates only). We can assume that the starting basis set  $\{\phi_i\}$  will in general be diabatic.  $U^d$  can then be diagonalized to yield the adiabatic surfaces  $W_i$  required for the Miller-George theory. In this approach the hypersurface  $W_i(R,r)$  is two-dimensional and one is required to know the analytic structure of a function of two complex variables, very often not an easy task. The second way is to use what is known as the vibronic representation. This approach makes use of (to begin with) a diabatic vibronic basis set

$$\phi_{in} = \phi_i(\vec{x}, r, R) \psi_n(r) \quad (IVb.3)$$

where  $\psi_n(r)$  is a vibrational wave function of  $BC$  independent of the electronic configuration of  $A$ . This set generates diabatic surfaces and couplings given by

$$U_{in,jm}^d = \langle \phi_{in} | -\frac{\hbar^2}{2\eta} \frac{\partial^2}{\partial r^2} + H_{el} | \phi_{jm} \rangle_{\vec{x}, r}, \quad (IVb.4)$$

which can again be diagonalized to produce adiabatic surfaces as required by the Miller-George treatment. The advantage here is that the adiabatic 'surfaces'  $W(R)$  here will only be functions of a single variable  $R$ , and their analytic structure is much



easier to handle than those of  $W_i(R, r)$ . Hence the classical nuclear problem is reduced to a one-dimensional one, and the result of the application of the Miller-George theory (IIIb.18) reduces to the Stuckelberg solution given by (IIc.9) to (IIc.14). In this subsection we will use the vibronic representation.

The DIM formalism applied to the collinear model (IVb.1) yields a two-by-two form for the electronic Hamiltonian:

$$U_{ii}^d(R, r) = v(r) + D + A_i(R-r/2) + A_i(R+r/2) + i\lambda/3, \quad i=1,2 \quad (\text{IVb.5a})$$

$$U_{12}^d = U_{21}^d = \sqrt{2} \lambda/3 \quad (\text{IVb.5b})$$

where  $D$  is the depth of the Morse well  $v(r)$ , the  $A_i$ 's are the anti-Morse functions, and  $\lambda$  is the spin-orbit coupling of  $X$ .  $U^d$  can be diagonalized to yield the adiabatic electronic surfaces  $W_i(R, r)$  with the accompanying adiabatic basis set  $\{\phi_i^a\}$  such that

$$H_{el} \phi_i^a(r, R, \vec{x}) = W_i(R, r) \phi_i^a(r, R, \vec{x}) . \quad (\text{IVb.6})$$

We prefer to use the representation [compare with (IVb.3)]

$$\Phi_{in} = \phi_i^a(\vec{x}, r, R) \psi_n(r) , \quad (\text{IVb.7})$$

where the vibrational wavefunctions  $\psi_n(r)$  are Morse functions satisfying the equation

$$\left\{ -\frac{\hbar^2}{2\eta} \frac{\partial^2}{\partial r^2} + v(r) \right\} \psi_n(r) = \epsilon_n \psi_n(r) . \quad (\text{IVb.8})$$

where  $\epsilon_n$  is the asymptotic vibrational energy for the  $n$  vibrational state of  $H_2$ . Using (IVb.4) and first integrating over the electronic coordinates  $\vec{x}$ , we can write

$$U_{in, jm}^d = \delta_{ij} \langle \psi_n | -\frac{\hbar^2}{2\eta} \frac{\partial^2}{\partial r^2} + W_i(R, r) | \psi_m \rangle_r - \frac{\hbar^2}{2\eta} \langle \psi_n | \zeta_{ij}(r, R) | \psi_m \rangle_r - \frac{\hbar^2}{\eta} \langle \psi_n | \chi_{ij}(r, R) \frac{\partial}{\partial r} | \psi_m \rangle_r , \quad (\text{IVb.9})$$

where

$$\zeta_{ij}(r, R) = \langle \phi_i^a(\vec{x}, r, R) | \frac{\partial^2}{\partial r^2} \phi_j^a(\vec{x}, r, R) \rangle_{\vec{x}} , \quad (\text{IVb.10})$$

$$\chi_{ij}(r, R) = \langle \phi_i^a(\vec{x}, r, R) | \frac{\partial}{\partial r} \phi_j^a(\vec{x}, r, R) \rangle_{\vec{x}}. \quad (\text{IVb.11})$$

These coupling matrix elements are similar to the nonadiabatic couplings  $T_{ij}^I$  and  $T_{ij}^II$  [(IB.11) and (IB.12)] discussed in Section Ib.

We can also show that

$$\chi_{ij} = -\chi_{ji} \quad (\text{IVb.12a})$$

$$\zeta_{ij} = \sum_{k=1}^2 \chi_{ik} \chi_{kj} + \partial \chi_{ij} / \partial r. \quad (\text{IVb.12b})$$

The couplings  $\chi$  and  $\zeta$  can furthermore be expressed in terms of  $U^d$ :

$$\chi_{12} = \sum_{ij} \Gamma_{1i} \Gamma_{2j} \frac{(\partial U_{ij}^d / \partial r)}{W_2 - W_1}, \quad (\text{IVb.13})$$

where

$$\Gamma_{11} = \Gamma_{22} = \frac{U_{12}^d}{[(W_1 - U_{11}^d)^2 + (U_{12}^d)^2]^{1/2}} \quad (\text{IVb.14a})$$

$$\Gamma_{12} = -\Gamma_{21} = \frac{U_{12}^d}{[(W_2 - U_{11}^d)^2 + (U_{12}^d)^2]^{1/2}}. \quad (\text{IVb.14b})$$

The 'diabatic' vibronic potential surfaces can then be written, from (IVb.9):

$$U_{in,im}^d(R) = \langle \psi_n | -\frac{\hbar^2}{2\eta} \frac{\partial^2}{\partial r^2} + W_i + \frac{\hbar^2}{2\eta} \chi_{12}^2 | \psi_m \rangle_r. \quad (\text{IVb.15a})$$

The off-diagonal matrix elements become:

$$U_{1n,2m}^d(R) = \frac{\hbar^2}{2\eta} \langle \psi_n | 2\chi_{12} \frac{\partial}{\partial r} + \frac{\partial \chi_{12}}{\partial r} | \psi_m \rangle_r. \quad (\text{IVb.15b})$$

For a particular vibrational transition  $n \rightarrow m$ , we have a one-dimensional two-state problem, i.e., we just have to deal with the  $2 \times 2$  matrix (IVb.15) with fixed  $n$  and  $m$ . This matrix can be diagonalized to yield the final adiabatic vibronic surfaces  $W_i^a(R)$  and the S-matrix is given directly in terms of the Stuckelberg solution [(IIc.9) to (IIc.14)]. Figure 3 illustrates the diabatic and adiabatic vibronic curves and the coupling  $\chi_{12}$  for the  $\text{BrH}_2$  system. The potential curves correlate asymptotically to the states 11 and 20.

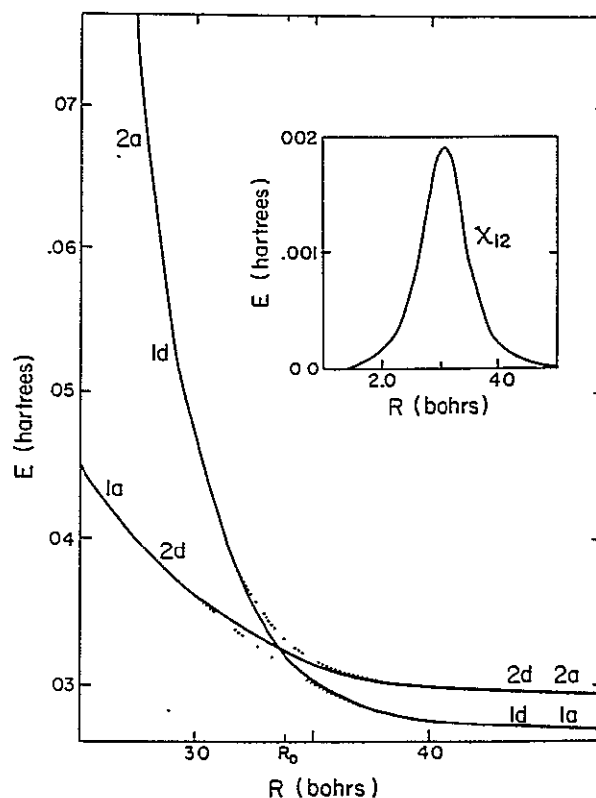


Fig. 3. The diabatic vibronic curves (the solid lines labelled ld and 2d) are split by the vibrational nonadiabatic coupling  $\chi_{12}$  (see insert) into the adiabatic vibronic curves, labelled la and 2a, which are represented by the dotted lines. Note that the labelling is reversed inside the avoided crossing.

As mentioned before, the formula  $p=\exp(-2\delta)$  very often does not yield good results for  $P=|S|^2$  when compared with quantum mechanical calculations; and the Nikitin correction formula (IIIId.13) is usually employed. There is, however, no cut and fast rule regarding the applicability of the Nikitin formula, it being exact only for exponential diabatic curves and couplings. In the present example, this formula has been applied to Morse-like potentials (IVb.5), and found to help appreciably in bringing the results into good agreement with quantum calculations.

Another slightly disconcerting factor in the application of the semiclassical approach is the difficulty with the phase factor  $\xi$  in (IIc.14). The value  $\pi/4$  is not often quoted and used in the literature. In the present applications, since the Nikitin correction formula is used, the form as given by (IIc.14)

would be rendered less rigorous, and the justification for its use in conjunction with the Nikitin formula requires more work. (In any case the use of this form is not very frequently reported in the literature). In our work we have varied  $\xi$  between  $-\pi/4$  and  $\pi/4$  to compare with quantum mechanical results. Reasonable agreements are achieved at either extreme, but it is found that  $\xi \sim \pi/10$  would shift the results into phase most closely with the quantum results.

In Figures 4 and 5 we present some results for  $|S_{1n,2m}|^2$  (written  $n_1 \rightarrow m_2$ ) for  $X = \text{Br}$ . In each case the semiclassical results are compared with exact quantum mechanical coupled-channel calculations. The reasonable agreement is apparent, pointing to the reliability of semiclassical calculations. Similar results are obtained for the  $\text{Br-H}_2$   $2_1-1_2$  and  $\text{F-H}_2$   $0_1-0_2$  transitions. It should be noted here that the distinct oscillatory behavior may be due entirely to the artifact of the collinear model. In three-dimensional calculations where there is strong coupling between translation and the various internal degrees of freedom, and especially when averages over a large number of quantum states are involved, the interference effects may be quenched.

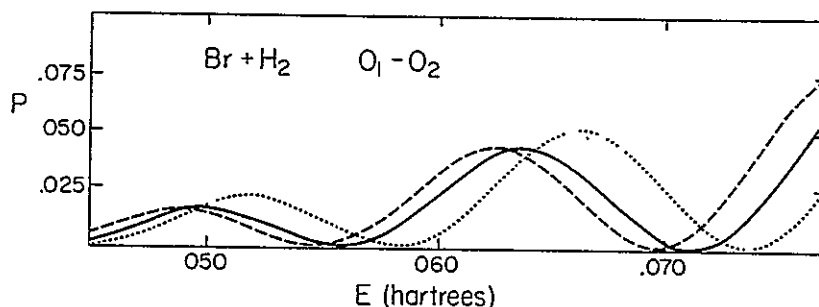


Fig. 4. Transition probability versus energy curves for the  $0_1-0_2$  transition in the  $\text{Br} + \text{H}_2$  collision system. The threshold for this transition is 0.027 hartree. The solid curve represents quantum results, and the dashed and dotted curves are the semiclassical results obtained with the phase factor  $\xi=0$  and  $+\pi/4$ , respectively.

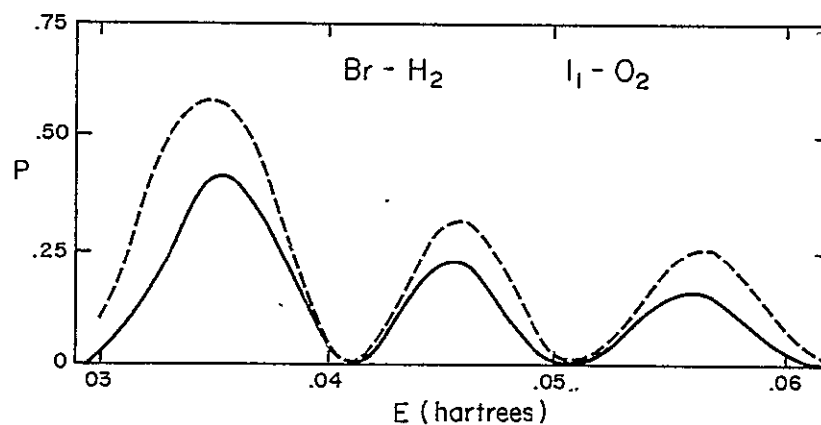


Fig. 5. Transition probability for the  $1_1-0_2$  transition in the  $\text{Br} + \text{H}_2$  collision system. The threshold for this transition is 0.029 hartree. The solid curve represents quantum results, and the dashed curve is the semiclassical result obtained using the phase factor  $\xi = -\pi/4$ .

## V. THEORY OF INTERACTION WITH FIELDS - LASER-ENHANCED COLLISIONS

The widespread interest in lasers has generated a quest for a deeper understanding of the effects of intense radiation on molecular collision processes. In this class of phenomena, as distinct from its atomic counterparts, dynamic considerations play a major role, and field-induced molecular events do not have to satisfy strict resonance requirements. Thus the radiation field may be expected to have very prominent effects on the collision dynamics. In particular, such molecular processes as collisional excitation, unimolecular dissociation, radiative collisions, and Penning and associative ionization are expected to be strongly influenced by an intense laser field. In this section we will generalize the Miller-George theory to include radiation interaction.

As soon as a field is put in, many problems suggest themselves. If we are dealing with a laser, the field may approach being monochromatic but always not exactly so. Even a single mode laser has a spectral linewidth owing to broadening effects such as Doppler, collision and radiative lifetime broadening. How many modes of the laser field must one include in the interaction Hamiltonian? This immediately raises the question of what the best representation is for the description of the photon field in laser-molecule interactions. There are a number of candidates: the Fock (photon-number) state representation, the coherent representation, or even the classical field approach, i.e., regarding the field simply as a time-dependent driving force on the system. What part does the polarization of the field play in laser-influenced molecular collisions? Recently there is even some controversy regarding the fundamental validity of using the ' $\vec{p} \cdot \vec{A}$ ' vis a vis the ' $\vec{p} \cdot \vec{E}$ ' interaction under the dipole approximation. These and other questions have not as yet been answered definitively. In this section we will restrict ourselves to the simplest possible (although not entirely realistic) situation of a monochromatic field interacting with a two-electronic state molecular system. The dipole approximation is assumed, and the photon-number representation is used, as this lends itself most easily to physical interpretation. Also, complications deriving from the intrinsic angular momentum of the photon will not be considered. Even under these limitations, the radiation field can be demonstrated to have significant effects on the collision system.

### Va. The Electronic (Vibronic)-Field Representation

The field-free collision system can be described by the electronically adiabatic potential surfaces  $W_i(\vec{R})$  which satisfy:

$$H_{el} \phi_i(\vec{R}, \vec{x}) = W_i(\vec{R}) \phi_i(\vec{R}, \vec{x}) \quad (\text{Va.1})$$

where  $\{\phi_i\}$  is the adiabatic basis set, and  $\vec{R}$  ( $\vec{x}$ ) are the nuclear (electronic) coordinates. One can also work with the vibronic surfaces  $W_i^1(R)$  as discussed in Section IVb, where  $R$  represents the translational degree of freedom only. Our discussion in what follows can be phrased equivalently in the electronic or vibronic representations; for the sake of definiteness, we will choose the former. The Hamiltonian due to the presence of the field is given by

$$\begin{aligned} H_f &= \hbar\omega\hat{a}^\dagger\hat{a} + \vec{\mu}(\vec{R},\vec{x}) \cdot \vec{E}_0'(\omega) (\hat{a}^\dagger + \hat{a}) \\ &\equiv \hbar\omega\hat{a}^\dagger\hat{a} + H_1. \end{aligned} \quad (\text{Va.2})$$

The first term represents the free-field Hamiltonian and the second term,  $H_1$ , the interaction Hamiltonian under the dipole approximation. It is understood that the photon creation and annihilation operators,  $\hat{a}^\dagger$  and  $\hat{a}$  respectively, are those for the single frequency  $\omega$ ; and

$$E_0'(\omega) = (2\pi\hbar\omega/V)^{1/2}\hat{e} \quad (\text{Va.3})$$

where  $V$  is the quantization volume of the collision system and  $\hat{e}$  is the unit polarization vector of the external field.

A natural basis set to be used for the matter-field system consists of states of the form  $\phi_i|n\rangle$ , where  $|n\rangle$  is the Fock state with  $n$  photons (of frequency  $\omega$ ), since they describe the asymptotic ( $R \rightarrow \infty$ ) configuration of the matter-field system. For instance one may visualize that before collision, the molecular system is in the  $i^{\text{th}}$  electronic state, while there are  $n_i$  photons floating around in the external field (in the quantization volume  $V$ ). This state of affairs is described by the asymptotic state  $\phi_i|n_i\rangle$ . After the collision, again at asymptotic regions, the molecular system may end up in a different electronic state (say the  $j$ ) whereas the number of photons in the external field may be changed to  $n_f$ . The final asymptotic state will then be described by  $\phi_j|n_f\rangle$ , and the S-matrix element corresponding to this process may be written  $S_{jn_f, in_i}$ . If  $n_j > n_i$ , stimulated emission

has taken place; if  $n_j < n_i$ , absorption has occurred.

Even though  $\{\phi_i\}$  is adiabatic in the field-free Hamiltonian  $H_{el}$ , the states  $\phi_i|n\rangle$  will no longer be adiabatic in the Hamiltonian  $H_{el} + H_f$ , since the interaction Hamiltonian  $H_1$  mixes them. They are only eigenstates of the Hamiltonian

$$H_R = H_{el} + \hbar\omega\hat{a}^\dagger\hat{a}, \quad (\text{Va.4})$$

$$H_R \phi_i|n\rangle = (W_i + n\hbar\omega) \phi_i|n\rangle. \quad (\text{Va.5})$$

The potential surfaces  $W_i + n\hbar\omega$  can now be considered the diabatic surfaces in the presence of the field. Analogous to the field-

free case, at locations (along  $\vec{R}$ ) where resonance occurs ( $W_i + n_i \hbar \omega = W_j + n_j \hbar \omega$ ), avoided crossings may be produced if symmetry conditions permit, i.e., if

$$\int d^3x \phi_j^* \vec{\mu}(\vec{x}, \vec{R}) \phi_i \neq 0. \quad (\text{Va.6})$$

In such cases, one may generate adiabatic curves just as one does in the field-free situation. These adiabatic curves  $E_i(\vec{R})$  satisfy the equation

$$(H_{el} + H_F) \psi_i(\vec{R}, \vec{x}) = E_i(\vec{R}) \psi_i(\vec{R}, \vec{x}) \quad (\text{Va.7})$$

where

$$\psi_i(\vec{R}, \vec{x}) = \sum_{\ell, n} \alpha_{i\ell n}(\vec{R}) \phi_\ell(\vec{R}, \vec{x}) |n\rangle. \quad (\text{Va.8})$$

The representation  $\psi_i$  is termed the electronic-field representation while  $E_i(\vec{R})$  is known as an electronic-field surface. The  $E_i$ 's are, of course, eigenvalues of  $H = H_{el} + H_F$ , where  $H$  is expressed in the  $\phi_i |n\rangle$  representation. Suppressing  $i$  in (Va.8) (i.e., writing it as a general eigenvector) and substituting in (Va.7), we obtain the infinite set of coupled equations for  $\alpha_{\ell n}$ :

$$E \alpha_{\ell n} = (W_\ell + n \hbar \omega) \alpha_{\ell n} + \sum_i d'_{\ell i} [\sqrt{n+1} \alpha_{i, n+1} + \sqrt{n} \alpha_{i, n-1}], \quad (\text{Va.9})$$

where

$$d'_{\ell i}(\vec{R}) = \vec{E}_0(\omega) \cdot \int d^3x \phi_\ell^*(\vec{R}, \vec{x}) \vec{\mu}(\vec{R}, \vec{x}) \phi_i(\vec{R}, \vec{x}) \quad (\text{Va.10})$$

is the dipole coupling between  $\phi_\ell$  and  $\phi_i$ . In obtaining (Va.9) we have used the following properties of the number states  $|n\rangle$ :

$$\langle n | \hat{a} | 0 \rangle = 0 \quad (\text{Va.11a})$$

$$\langle n' | \hat{a} | n'' \rangle = \sqrt{n''} \delta_{n', n''-1} \quad (\text{Va.11b})$$

$$\langle n' | \hat{a}^\dagger | n'' \rangle = \sqrt{n''+1} \delta_{n', n''+1}. \quad (\text{Va.11c})$$

These properties lead to the important fact that only states  $\phi_i |n\rangle$  with a difference in photon number equal to one are directly coupled; and hence, to first order in the dipole strength  $d'$ , only single-photon processes are possible when the interaction term proportional to  $\vec{A}^2$  is ignored ( $\vec{A}$  is the field vector potential). Even with this simplification, (Va.9) shows that, in order to obtain the adiabatic (electronic-field) surfaces, an infinite-dimensional matrix has to be diagonalized in general.



## Vb. The Rotating-Wave Approximation (RWA)

For the present discussion we limit ourselves to the two-state molecular system with  $W_2 > W_1$ . In this molecular collision problem, the energy detunings  $\Delta_{\pm}$  for a transition  $\phi_1|n\rangle \leftrightarrow \phi_2|n\pm 1\rangle$

$$\Delta_{\pm}(\vec{R}) = W_2 - W_1 \pm \hbar\omega, \quad (\text{Vb.1})$$

must be examined as a function of all the nuclear degrees of freedom. For  $W_2 > W_1$ ,  $\Delta_{+} > \hbar\omega$  for all  $\vec{R}$ ; hence the transition  $\phi_1|n\rangle \rightarrow \phi_2|n+1\rangle$  can be considered anti-resonant (or potential energy non-conserving).  $\Delta_{-}$ , however, may vanish for certain nuclear configurations, implying that the transition  $\phi_1|n\rangle \rightarrow \phi_2|n-1\rangle$  is resonant at those configurations.

We now assume that  $d'_{11}=0$  (which would be rigorously true for a homonuclear atom-atom collision system). In this case the secular matrix for (Va.9) block-diagonalizes, and it can be written in the general form shown in (Vb.2), where the coupling strength is

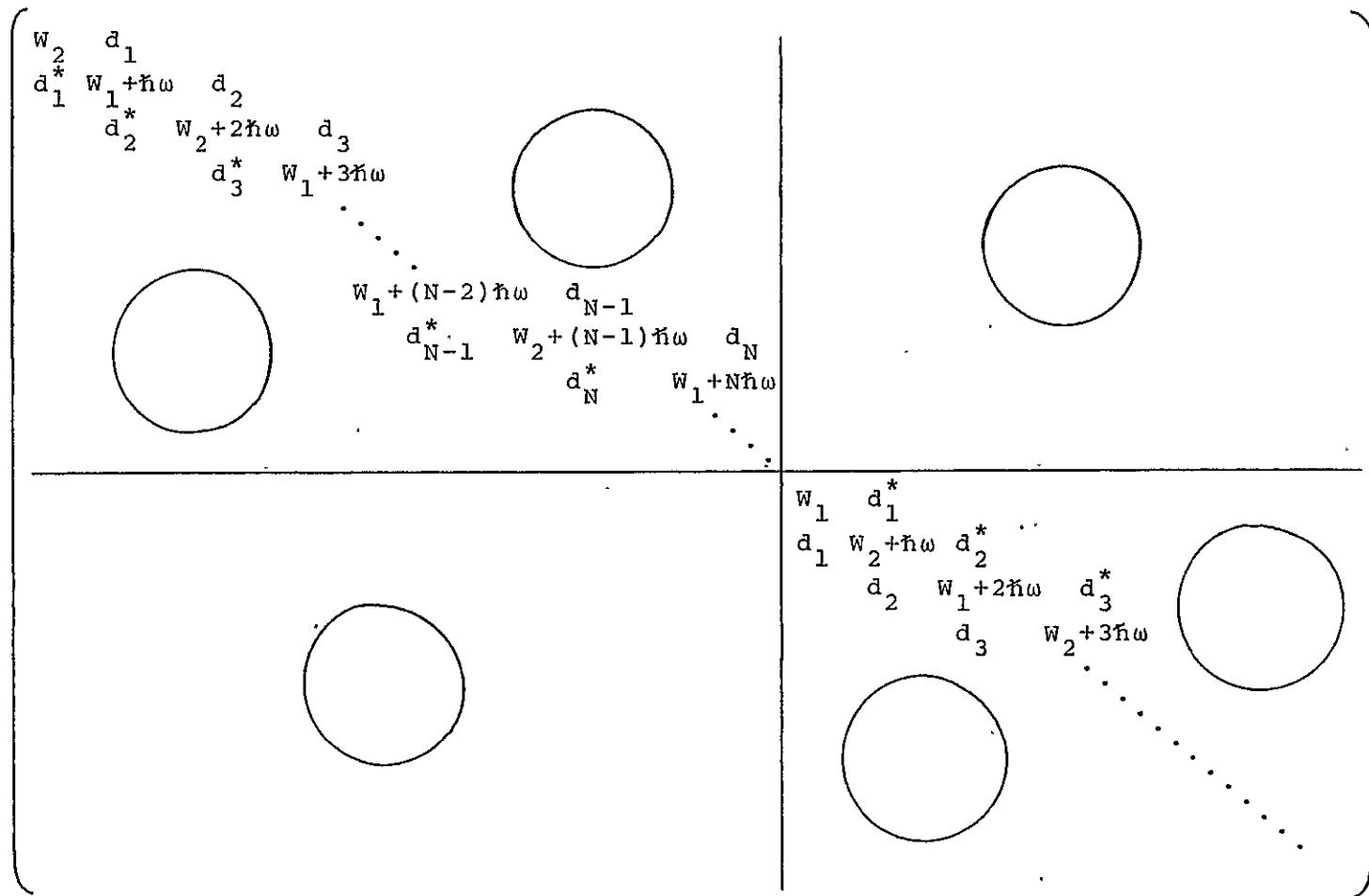
$$d_N = \sqrt{N} d'_{21} = \vec{E}_0 \cdot \int d^3x \phi_2^* \vec{\mu} \phi_1. \quad (\text{Vb.3})$$

$N$  is the number of photons in the external field and  $\vec{E}_0$  is the electric field strength. The block diagonalization reflects the fact that, in making the transition  $\phi_1 \leftrightarrow \phi_2$ , the system must gain or lose an odd number of photons. The two non-diagonal blocks are completely equivalent; and depending on the initial conditions of the collision environment, one can ignore the appropriate one. For instance, if the collision system is prepared in the state  $\phi_1$  and the applied radiation field has field strength

$$E_0 = \sqrt{2\pi N \hbar \omega / V} \quad (\text{IVb.4})$$

with  $N$  odd, then we can work entirely with the upper left block; and with  $N$  even, the lower right block. In practice, of course,  $N$  is so large that  $d_N \sim d_{N+1} \sim d_{N-1}$ , and the two blocks would be largely equivalent.

It is in principle possible for a system prepared in  $\phi_1$  initially to absorb  $n$  photons ( $n$  odd  $\leq N$ ) or emit  $n$  photons ( $1 \leq n$  odd  $< \infty$ ), and either stay in  $\phi_1$  or make a transition to  $\phi_2$ . While processes involving transitions  $\phi_1|n_1\rangle \leftrightarrow \phi_2|n_2\rangle$  may or may not be resonant if  $n_2 < n_1$ , they will always be anti-resonant if  $n_2 > n_1$ . The RWA in the collision case (similar to the atomic case) consists in throwing away all direct couplings between diabatic states  $\phi_1|n\rangle$  of the latter kind ( $n_2 > n_1$ ); for example, between the states  $\phi_2|N-1\rangle$  and  $\phi_1|N-2\rangle$ . It is expected to be



less accurate when the applied field strength is very large; or in non-resonant situations (as opposed to anti-resonant ones) corresponding to  $\phi_1|N\rangle \rightarrow \phi_2|N-1\rangle$  such that the energy detuning,  $W_2 - W_1 - \hbar\omega$ , is not significantly different from that for the anti-resonant transition,  $W_2 - W_1 + \hbar\omega$ . In the latter instance, application of the RWA would not be internally consistent, since it would not be justifiable to chop only couplings connecting states with  $n_2 > n_1$  while keeping those with  $n_1 > n_2$  if the detunings are roughly equal for the two cases.

In our example of the two-state model, the RWA then leads to complete block diagonalization of (Vb.2) into independent  $2 \times 2$  matrices. For the initial conditions mentioned previously one has to consider only the diabatic matrix

$$\begin{pmatrix} W_2 + (N-1)\hbar\omega & d_N \\ d_N & W_1 + N\hbar\omega \end{pmatrix}. \quad (\text{Vb.5})$$

Diagonalization of (Vb.5) will lead to the two adiabatic (electronic-field) surfaces

$$E_{1,2} = N\hbar\omega + \frac{W_1 + W_2 - \hbar\omega}{2} \pm \frac{1}{2}[(W_2 - W_1 - \hbar\omega)^2 + 4d_N^2]. \quad (\text{Vb.6})$$

[Compare with (IIId.1)]. In effect the RWA limits the consideration of absorption and emission to single-photon resonant processes. Figure 6 illustrates the construction of the electronic-field surfaces.

#### Vc. An Example

To apply the Miller-George theory,  $E_{1,2}$  are considered as analytic functions of  $\vec{R}$ . As discussed before they can be regarded as different Riemann sheets of the single analytic function  $E(\vec{R})$ , with branch points which are roots of the equation

$$E_1(\vec{R}) = E_2(\vec{R}), \quad (\text{Vc.1})$$

or

$$[W_2(\vec{R}) - W_1(\vec{R}) - \hbar\omega]^2 + 4d_N^2(\vec{R}) = 0. \quad (\text{Vc.2})$$

Classical trajectories can be propagated on  $E(\vec{R})$ , as described before, making transitions by rounding the appropriate branch points.

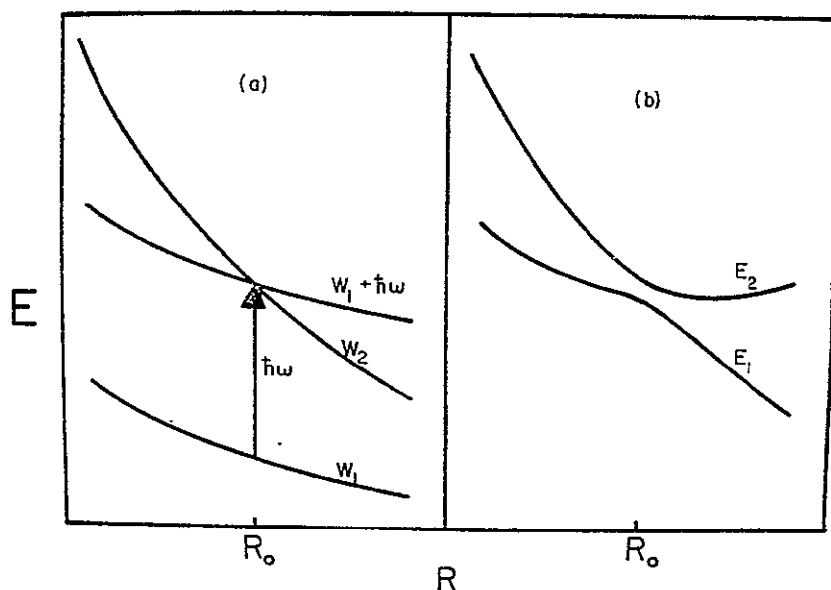
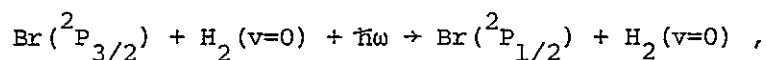


Fig. 6. (a) Schematic drawing of two field-free adiabatic surfaces  $W_1$  and  $W_2$  as functions of the translational coordinate  $R$ .  $R_0$  is the point at which the field is in resonance with the two surfaces. (b) Schematic drawing of the electronic-field-surfaces  $E_1$  and  $E_2$ . The splitting between them at  $R_0$  is caused by the radiative coupling  $d_N$ .

We again consider an example of collinear A+BC collision. The specific process is



(Vc.3)

where  $v$  designates the vibrational state of  $\text{H}_2$ .  $W_1$  and  $W_2$  are taken to be vibronic potential surfaces as before (see section IVb) so that nuclear motion is reduced to one-dimensional. The interaction of the field with the molecular system is approximated by the interaction with the asymptotic collision species alone. In this case the magnetic dipole transition matrix element for the halogen dominates. Hence the magnetic field of the

laser radiation appears for  $\vec{E}_0$  (formerly considered to be the electric field) in all expressions. The value of  $\sqrt{4/3}$  a.u. (atomic units) is used for the magnetic dipole transition moment  $|\vec{\mu}_{12}|$ . (This value actually holds for all halogens).  $\hbar\omega$  is chosen to be 1.001 times the Br spin-orbit splitting (0.4568 eV), such that the laser cannot induce a spin-orbit transition without the aid of the  $H_2$  collision partner. A field strength  $E_0$  of  $5.1 \times 10^6$  V/cm ( $10^{-3}$  a.u.) is used. The vibronic-field surfaces (curves in the present case) can be constructed according to (Vb.6), where  $W_{1,2}$  and  $E_{1,2}$  resemble the schematic drawings of Figure 6.

Since this is a one-dimensional problem, the Stuckelberg solution (IIc.9) to (IIc.14) again applies, with the slight alteration that  $W_i$  in these equations are replaced by  $E_i$ . A pair of complex intersection points between  $E_1$  and  $E_2$  is located at  $R_* = 4.01 \pm 0.422i$  bohr (1 bohr = 0.529 Å), and classical trajectories were integrated in the complex plane which switch curves smoothly at the intersection point. The Nikitin correction formula (IIId.13) is again employed and  $\xi$  is chosen to be  $\pi/4$ . The semiclassical results are compared with the quantum mechanical as well as the field-free results in Figure 7. The high probabilities for the laser-induced process are in direct contrast to small probabilities for the same process in the absence of the field. The field-free process tends to be electronically adiabatic and the field is the sole agent in inducing electronically nonadiabatic transitions in the present case.

## VI. MISCELLANEOUS TOPICS IN THE THEORY OF LASER-ENHANCED COLLISIONS

The majority of collision processes only require a finite number of states (usually two) for their description. There are, however, some in which one or more discrete states of a system can interact with the continuous spectrum. There are in general known as bound-continuum processes. In these processes one is interested in the S-matrix element connecting an initial discrete state and a final continuum channel; and very often there is no straightforward way to reduce the problem to a finite-state one or even one involving infinitely many discrete states. In this section we discuss two examples of field-induced bound-continuum collision processes, spontaneous emission and Penning ionization, in which S-matrix elements may be calculated using discrete-problem techniques by the introduction of certain approximations and discretization procedures. The formalisms for both problems still leave much room for rigorous justification and improvement, and may not be adaptable to the most general collision situations. However, they do provide convenient descriptions, both intuitively and physically, of the respective processes. Our discussion of the bound-continuum

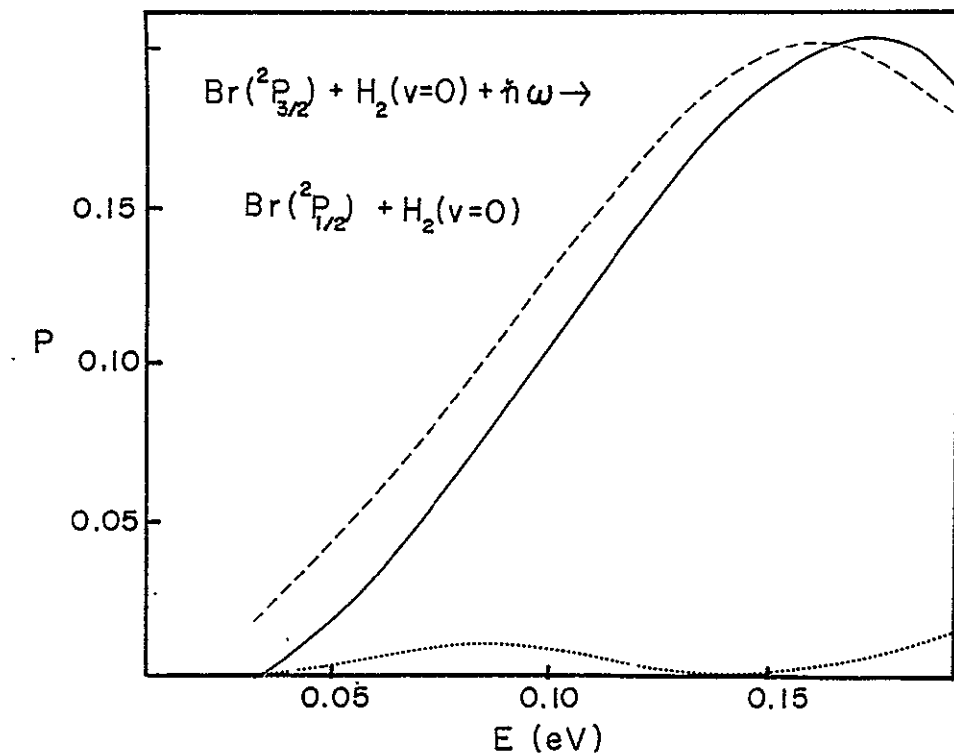


Fig. 7. Probabilities for the collinear reaction  $\text{Br}(^2P_{3/2}) + \text{H}_2(v=0) + \hbar\omega \rightarrow \text{Br}(^2P_{1/2}) + \text{H}_2(v=0)$  as functions of initial relative translational collision energy. The value of  $\hbar\omega$  is 1.001 times the asymptotic spin-orbit splitting. Shown are the results from the quantum calculations using the two-(vibronic) state model (solid line) and results from semiclassical calculations using the two-(vibronic) state model (dashed line). The quantum probabilities for the field-free transition (dotted line) have been multiplied by 100.

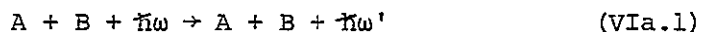
problems will be based on the Miller-George semiclassical formalism developed earlier, but we should mention that the discretization procedure introduced below for the ionization problem is also adaptable to a quantum mechanical coupled-channels treatment.

The semiclassical formalism we have developed in the present lecture series for discrete-state field-induced problems can be considered to be exact within the limitations of finite-dimensionality and the RWA. The treatment is non-perturbative, and collisional and radiative interactions are treated on the same footing. Despite these advantages, its application will often raise severe practical problems [e.g., in the analytic continuation of the potential surfaces and the location of branch points (seams)]. For this reason, simpler treatments often retain their appeal and value. In particular, time-dependent

perturbation treatments may be most useful when the laser field is of moderate strength and considered as a classical driving force. To conclude the present lecture series, we will give in Section VIc a description of such a theory applied to laser-induced collisional processes as due to Weiner.

#### VIa. Collision-Induced Spontaneous Emission

We consider non-reactive processes of the type



(e.g., the Br-H<sub>2</sub> system) where  $\omega$  is the frequency of the incident laser radiation and  $\omega'$  that of the emitted radiation. To describe the interaction of the collision system with the incident laser, we can make use of the electronic(vibronic)-field surfaces  $E_i$  introduced in Section Va and illustrated in Figure 6.

These electronic-field surfaces [arising from the diagonalization of (Vb.2)] can be regarded as forming a spectrum for spontaneous emission if radiative coupling with the vacuum field is now considered. This interaction involves in principle an infinity of field modes, since a continuum of emission frequencies is possible corresponding to the different nuclear configurations at which emission can take place. The symmetry allowed emission transitions between the electronic-field surfaces are illustrated in Figure 8 (both dotted and solid lines). If we consider the case where the system starting on  $W_1$  asymptotically is de-excited back to  $W_1$  asymptotically after sequential absorption and emission of photons, only the transition marked by the solid line (in Figure 8) need be considered.

The semiclassical picture allows us to think of the photon of frequency  $\omega'$  as being emitted near the configuration  $R_E$  such that

$$\hbar\omega' = E_2(R_E) - E_1(R_E) \quad (\text{VIa.2})$$

Emission-electronic-field surfaces  $E_+^{(e)}$  describing the dynamics of this event can then be constructed analogously to the electronic-field surfaces. These are illustrated in Figure 9. It should be noted that the dimensions of the emission avoided crossing are much smaller than those of the absorption one since the former is generated through coupling with the vacuum field. Referring to Figure 9(b), the dynamical picture then emerges that if the system is still propagating on the surface  $E_+^{(e)}$  at asymptotic regions, it will have emitted a photon of frequency  $\omega'$  and become de-excited to the ground state  $W_1$ .

The probability of emission at  $R_E$  is determined semiclassically by the trajectories which avoid emission before and which lead to emission when that configuration is reached. If we consider the case of discretized allowable emission configura-

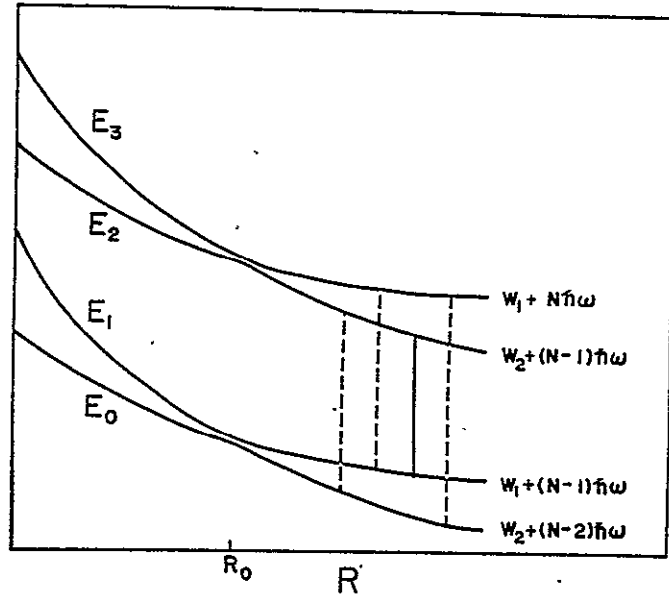


Fig. 8. Symmetry-allowed emission transitions in the two-state electronic field representation. The splitting at  $R_0$  is caused by the absorption radiative coupling. The solid line represents the de-excitation transition from  $W_2$  back to  $W_1$ .

tions (in practice, one needs to consider a continuum), a system propagating on the surface  $E_2$  after absorption will encounter a series of configurations at which it can emit. Let one of these be  $R_{ei}$ . At this configuration, the approximation is made that there is emission coupling only at the frequency  $\hbar\omega_i = E_2(R_{ei}) - E_1(R_{ei})$ . Couplings at frequencies corresponding to more distant configurations can be considered as yet not 'turned on'. Those at frequencies corresponding to configurations prior to  $R_{ei}$  are assumed to have negligible effects on the dynamics of the system at  $R_{ei}$ , since the system has 'survived' pre-emission loss at these configurations before reaching  $R_{ei}$ . Hence, at each possible emission configuration, emission-electronic-field surfaces can be generated independently of emission couplings at other configurations. A schematic representation for the discrete case



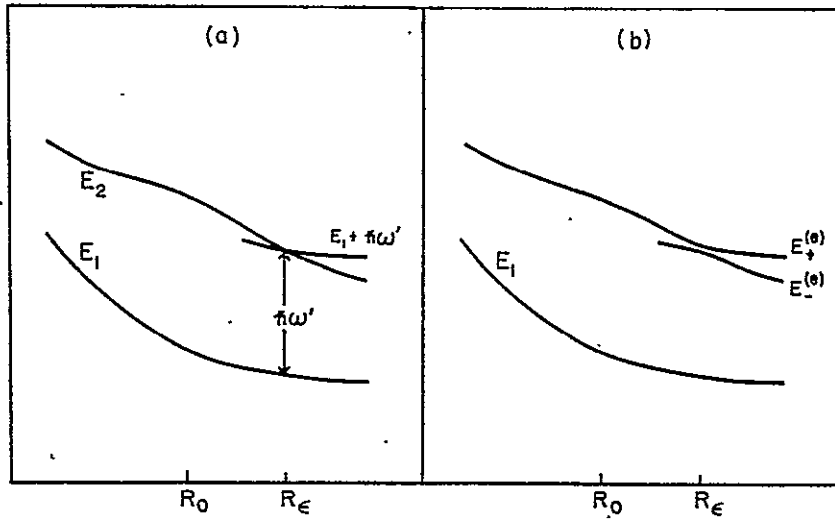


Fig. 9. (a) Schematic drawing of the diabatic surfaces for the description of single-mode emission at  $R_\epsilon$ . (b) Schematic drawing of emission-electronic-field surfaces for single-mode emission at  $R_\epsilon$ . The avoided crossing is caused by emission radiative coupling.

is illustrated in Figure 10.

When the emission sites become continuously distributed along  $R$ , we still retain the approximation of treating each avoided crossing as generated by a localized emission coupling. In this continuous limit the discrete series of branch points will constitute a line of branch points in the complex  $R$ -plane. It will be expected to be relatively close to the real axis compared to the location of the absorption branch point because of the relative weakness of the emission couplings. Whereas in the discrete case a trajectory, after rounding each emission branch point, may return to the real axis before going around the next, in the continuum case it will be forced to deviate from the real axis throughout the configurations at which emission coupling is active and be propagated along the line of branch points. The

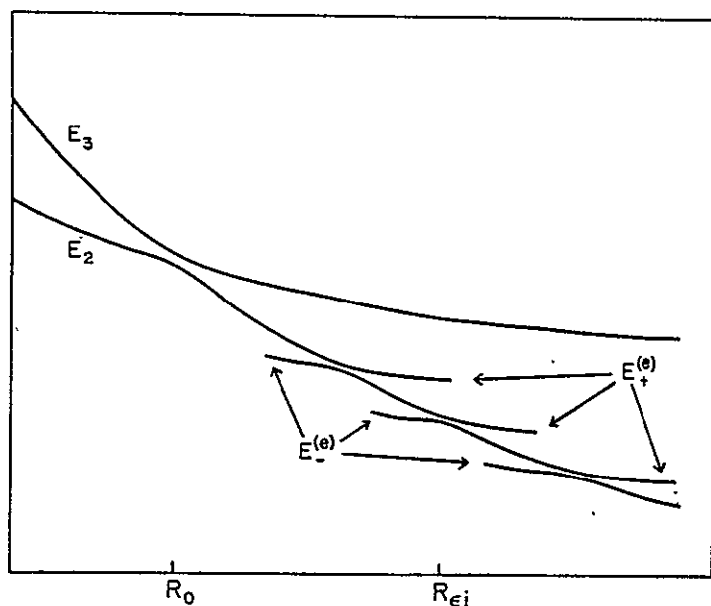


Fig. 10. Schematic drawing of emission electronic-field surfaces for discrete emission configurations.  $R_{ei}$  is the  $i$ th emission site.

imaginary action accumulated along this line will determine the accumulated probability for making local transitions from  $E_+^{(e)}$  to  $E_-^{(e)}$  continuously, that is, the accumulated probability for not having emitted a photon while the molecular system stays on  $E_2$ . At the actual emission site the trajectory reverts back to the real axis and is propagated to asymptotic regions on  $E_+^{(e)}$ .

The shape of the emission spectrum (as a function of the emission configuration  $R_e$ ) is then found to be determined by the shape factor

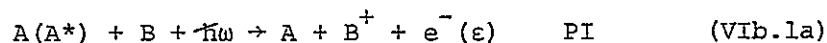
$$F_S(E, R_e) = \exp[-2\chi(E, R_e)] \{1 - \exp[-2\xi_e(E, R_e)]\} \quad (\text{VIa.3})$$

where  $E$  is the total energy of the collision system. The action factor  $\chi$  accounts for pre-emission effects and  $1 - \exp(-2\xi_e)$  is the

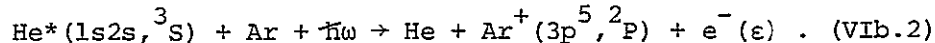
local emission probability. Since the emission branch points tend to depart more from the real axis as  $R_E$  increases,  $1 - \exp(-2\xi_E)$  will increase and  $\exp(-2\chi)$  decrease as  $R_E$  becomes large. Thus it is seen that pre-emission and localized actual emission effects compete with each other for the total emission probability at a particular configuration. Results of model calculations indicate, however, that this total probability depends critically only on the local emission probability at the actual emission configuration.

#### VIb. Laser-Induced Collisional Ionization

Let us consider non-reactive processes of the type



where  $\omega$  is the laser photon frequency,  $\epsilon$  is the kinetic energy of the emitted electron, and  $A(A^*)$  means that  $A$  may or may not be in an excited state. Processes (VIb.1a) and (VIb.1b) are the counterparts to field-free (FF) Penning ionization (PI) and associative ionization (AI) respectively. An example of (VIb.1a) is



There are basically two kinds of field-induced ionization processes: field-assisted (FA) and field-modified (FM). FA processes occur in cases where the electronic continuum would not have been energetically accessible in the absence of the field, whereas FM processes occur in cases where field-free ionization is already possible, the field serving to bring new regions of the electronic continuum into accessibility. (VIb.2) is an example of FM ionization. The system can be described by two potential curves:  $V_d$  for  $\text{He}^* + \text{Ar}$  and  $V_+$  for  $\text{He} + \text{Ar}^+$ .  $V_d$  is embedded in the electronic continuum of  $V_+$  and hence field-free ionization is possible. The introduction of the field enables new regions of the continuum to be accessible by collision, as illustrated in Figures 11 and 12. From these figures the qualitative picture emerges that there will be three peaks in the emitted-electron energy spectrum of the cross-section. The middle one is the field-free one, whereas the other two are field-induced, separated from each other by  $2\hbar\omega$ .

In the field-free case the bound-continuum aspect of the problem consists of the fact that the discrete state  $|\phi_d\rangle$ , corresponding to the surface  $V_d$ , can interact with the continuum of states  $|\phi_+, \epsilon\rangle$  corresponding to the surfaces  $V_+ + \epsilon$ , where  $\epsilon$  is an arbitrary electronic energy. Any discretization procedure amounts to replacing the infinite set of continuum states  $|\phi_+, \epsilon\rangle$

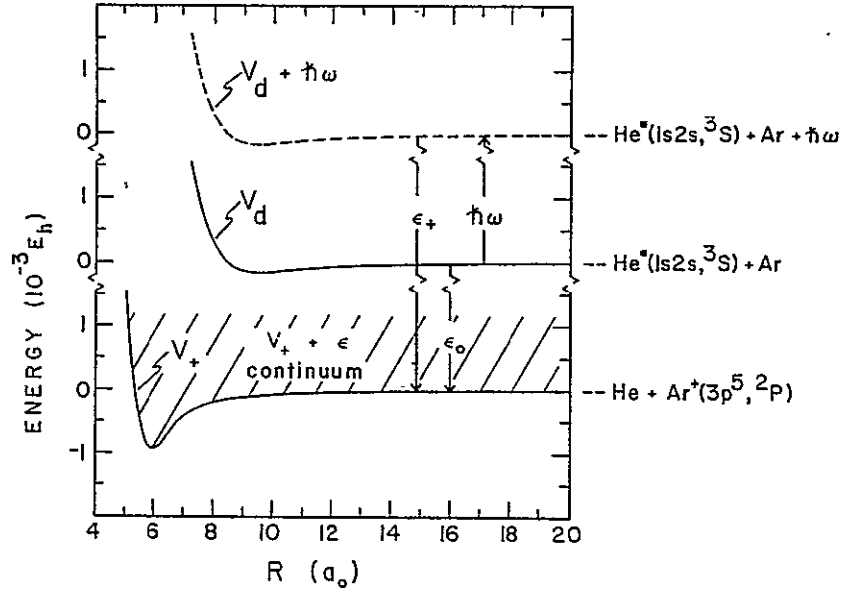


Fig. 11. Relevant potential energy curves for  $\text{He}^* + \text{Ar} + \hbar\omega$  collisions. Emission of an electron with energy  $\epsilon_+$  requires absorption of a photon.

by an infinite set of discrete states  $|\phi_+, \tilde{\epsilon}\rangle$ , such that the Coulomb couplings,  $V_{d\tilde{\epsilon}}$  and  $V_{d\tilde{\epsilon}}$ , leading to ionization are related by

$$V_{d\tilde{\epsilon}} = \int_0^\infty d\epsilon \, a_{\tilde{\epsilon}}(\epsilon) V_{d\epsilon} , \quad (\text{VIb.3})$$

where

$$a_{\tilde{\epsilon}}(\epsilon) = \langle \phi_+, \epsilon | \phi_+, \tilde{\epsilon} \rangle . \quad (\text{VIb.4})$$

$a_{\tilde{\epsilon}}(\epsilon)$  must satisfy the orthonormality condition

$$\int_0^\infty d\epsilon \, a_{\tilde{\epsilon}}^*(\epsilon) a_{\tilde{\epsilon}'}(\epsilon) = \delta_{\tilde{\epsilon}\tilde{\epsilon}'} , \quad (\text{VIb.5})$$



$$\tilde{V}^{(L)} = \begin{pmatrix} V_d^{(L)} & V_{d\tilde{\epsilon}} \\ V_{d\tilde{\epsilon}}^* & V_+^{(L)} + \tilde{\epsilon} \end{pmatrix}, \quad (\text{VIb.7})$$

$$\text{where} \quad V_d^{(L)} = V_d + L(L+1)/2\mu R^2, \quad (\text{VIb.8})$$

$$V_+^{(L)} = V_+ + L(L+1)/2\mu R^2, \quad (\text{VIb.9})$$

and  $\mu$  is the reduced mass of the collision system. The coupling  $V_{d\tilde{\epsilon}}$  induces an avoided crossing where the curves  $V_d^{(L)}$  and  $V_+^{(L)} + \tilde{\epsilon}$  cross, and the S-matrix describing transition to a discretized state,  $S_{\tilde{\epsilon}}^{(L)}$ , can be computed by the semiclassical formalism described earlier. The S-matrix for transition to the true continuum is then given by

$$S_{\epsilon}^{(L)} = \int_{\tilde{\epsilon}} a_{\tilde{\epsilon}}(\epsilon) S_{\tilde{\epsilon}}^{(L)}. \quad (\text{VIb.10})$$

When a field is present, two new regions of the continuum are accessible. The first one is such that  $V_d^{(L)} + N\hbar\omega$  cross  $V_+^{(L)} + \tilde{\epsilon} + (N-1)\hbar\omega$ , and the second one such that  $V_d^{(L)} + N\hbar\omega$  cross  $V_+^{(L)} + \tilde{\epsilon} + (N+1)\hbar\omega$ . The new regions are such that both crossings occur where the (field-free) Coulomb coupling is dominated by the longer-ranged radiative coupling. Ionization in the first region requires absorption of a photon while ionization in the second region leads to emission of a photon. Semiclassical treatments can be applied to these field-induced cases entirely analogously to the field-free case.

#### VIc. Time-Dependent Perturbation Theory

Let us consider the following case of collisional excitation in the presence of a laser,

$$A^* + B + \hbar\omega \rightarrow A + B^{**}, \quad (\text{VIc.1})$$

where the asymptotic energy levels of the atoms A and B are illustrated in Figure 13. The formulation of the problem given below is due to Weiner.

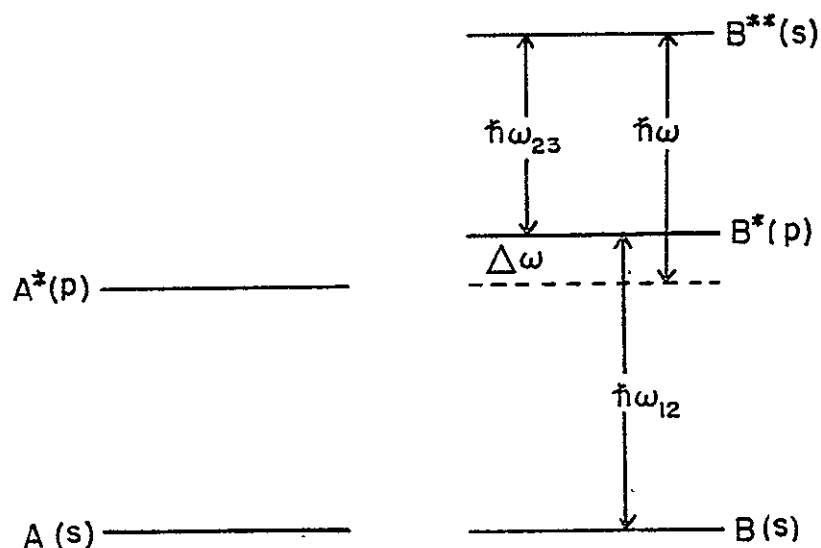


Fig. 13. Asymptotic energy levels of a diatomic collision. The dotted line represents a virtual atomic state of B.

A long-range dipole-dipole interaction between A and B produces a virtual B state at energy equal to the energy difference between A and  $A^*$ , which is a linear combination of the states corresponding to B and  $B^*$  (mixing s and p characters). Radiative coupling then carries the system from the virtual state to the final state  $B^{**}$ . Direct radiative coupling (dipole coupling) between B and  $B^{**}$  is symmetry forbidden (since both are S states). Both the dipole-dipole and the radiative dipole interactions are assumed to be weak so that perturbation theory can be applied. These interactions are respectively given by

$$H_{12} \approx \frac{\mu_A^{12} \mu_B^{12}}{R^3} \quad (\text{Vic.2})$$

$$H_{23} = E \mu_B^{23} \cos \omega t \quad (\text{Vic.3})$$

where E is the field strength of the laser and the  $\mu$  are the dipole moments of the respective atoms:

$$\mu_A^{12} = \langle A(s) | \mu | A^*(p) \rangle, \quad (\text{Vic.4a})$$

$$\mu_B^{12} = \langle B(s) | \mu | B^*(p) \rangle, \quad (\text{Vic.4b})$$

$$\mu_B^{23} = \langle B^*(p) | \mu | B^{**}(s) \rangle; \quad (\text{Vic.4c})$$

and R is the internuclear distance between A and B. The coupled equations (through second order) for the time-dependent expansion coefficients of the atomic wave function for B are ( $b_2^{(0)}=0$ ,  $b_3^{(0)}=0$ ):

$$\dot{b}_1^{(0)} = 0 \quad (\text{Vic.5})$$

$$\dot{b}_2^{(1)} = \frac{1}{i\hbar} b_1^{(0)} H_{12} e^{i\omega_{12}t} \quad (\text{Vic.6})$$

$$\dot{b}_3^{(2)} = \frac{1}{i\hbar} b_2^{(1)} H_{23} e^{i\omega_{23}t}. \quad (\text{Vic.7})$$

Putting  $b_1^{(0)}=1$  and using the straight line approximation  $R(t)=vt$  with impact parameter b, we have

$$\begin{aligned} b_2^{(1)} &= \frac{\mu_A^{12} \mu_B^{12}}{i\hbar} \int_0^\infty dt \frac{e^{i\omega_{12}t}}{(b^2 + v^2 t^2)^{3/2}} \\ &= \frac{2}{i\hbar} \frac{\mu_A^{12} \mu_B^{12}}{v^2 b} \omega_{12} K_1 \left( \frac{\omega_{12} b}{v} \right) \end{aligned}$$

asymptotically

$$\frac{2}{i\hbar} \left( \frac{\mu_A^{12} \mu_B^{12}}{v b^2} \right) \quad (\text{Vic.8})$$



where  $K_1$  is a first-order modified Bessel function and the asymptotic limit holds when  $\omega_{12}b/v \ll 1$ . Substituting (Vic.8) into (Vic.7) and using (Vic.3), we have

$$\dot{b}_3^{(2)} = -\frac{1}{\hbar^2} \frac{E \mu_A^{12} \mu_B^{12} \mu_B^{23}}{vb^2} e^{i\Delta\omega t} \quad (\text{Vic.9})$$

where the RWA has been applied and  $\Delta\omega \equiv \omega_{23} - \omega$ . Hence

$$b_3^{(2)} = -\frac{1}{i\hbar^2} \frac{E \mu_A^{12} \mu_B^{12} \mu_B^{23}}{(\Delta\omega) vb^2} (e^{i\Delta\omega t} - 1) , \quad (\text{Vic.10})$$

and the finite-time transition probability is given by

$$P(t) = |b_3^{(2)}|^2 = 2 \left( \frac{1}{\hbar} \frac{\mu_A^{12} \mu_B^{12}}{vb^2} \right)^2 \left( \frac{E \mu_B^{23}}{\hbar \Delta\omega} \right)^2 (1 - \cos \Delta\omega t) . \quad (\text{Vic.11})$$

$P(t)$  is proportional to  $E^2$ , i.e., linear with respect to the intensity of the radiation (implying a single-photon process).

## PROBLEMS

1. Using (Ib.4) to (Ib.8) verify (Ib.9), in which the matrix elements are given by (Ib.10) to (Ib.12).
2. Show that the diagonal elements of  $\tilde{\mathbf{P}}(k)$  [defined in (Ib.15)] vanish identically regardless of representation and that  $\tilde{\mathbf{P}}(k)$  is hermitian.
3. Verify (Id.24).
4. Give an approximate, perturbative derivation of the Landau-Zener formula [(IIa.8)] in the low velocity limit.
5. Following Stuckelberg's procedure write down the fourth-order differential equation for  $\chi_1$  [where  $\chi_1$  and  $\chi_2$  satisfy (IIc.1)]. Then assume a general WKB solution of the form (IIc.5) and obtain equations for  $S_0$  and  $S_1$  when coefficients of the powers of  $\hbar$  are separately equated to zero. Finally, retaining only  $S_0$  and  $S_1$  in the expansion (IIc.5) derive the general WKB solutions for  $\chi_1$  and  $\chi_2$ .
6. In the Meyer-Miller treatment establish the equivalence between Hamilton's equations of motion for the classical electronic degrees of freedom [(IIe.10b), (IIe.10c) and (IIe.10d)] and the time-dependent coupled equations (IIe.1) with the trajectory  $R(t)$  determined by Ehrenfest's theorem.
7. Show that for the three-state nonadiabatic transition problem the branch point structure of the adiabatic surfaces is still derived from square root functions.
8. Show that  $\tilde{\mathbf{C}}(R)$  [given by (Ib.25)] with  $\alpha$  given by (IIId.10) diagonalizes  $\tilde{\mathbf{U}}^d(R)$  as given by (IIId.7).
9. For a simple harmonic potential verify (IVa.7) and (IVa.8).
10. Verify (IVb.12), (IVb.13) and (IVb.14).
11. Write down an expression for the nonadiabatic transition S-matrix for the case of a one-dimensional two-state, two-intersection-point system.
12. Derive (Va.9).
13. Using the Miller-George theory in the context of the two-state electronic-field representation, show that in the weak field limit the local transition probability is proportional to the field intensity.

14. Assuming single-mode emission write down the matrix for the diabatic representation of the emission-electronic-field surfaces and simplify.
15. Verify (VIb.3) and (VIb.5).

#### KEY REFERENCES

1. Y. N. Demkov: 1964, Sov. Phys. JETP 18, pp.138-142.
2. T. F. George, I. H. Zimmerman, P. L. DeVries, J. M. Yuan, K. S. Lam, J. C. Bellum, H. W. Lee, M. S. Slutsky and J. T. Lin, in " Chemical and Biochemical Applications of Lasers ", Vol. IV, edited by C. B. Moore ( Academic Press, New York, 1979 ), pp.253-354.
3. H. -D. Meyer and W. H. Miller: 1979, J. Chem. Phys. 70, pp.3214-3223.
4. W. H. Miller: 1974, Adv. Chem. Phys. 25, pp.69-177.
5. W. H. Miller and T. F. George: 1972, J. Chem. Phys. 56, pp.5637-5652.
6. E. E. Nikitin, " Theory of Elementary Atomic and Molecular Processes in Gases " ( Clarendon Press, Oxford, 1974 ).
7. F. T. Smith: 1969, Phys. Rev. 179, pp. 111-123.
8. J. C. Tully and R. K. Preston: 1971, J. Chem. Phys. 55, pp.562-572.

1. CHANGE NO. 1-21	2. DATE ISSUED 1-11-80	3. DOCUMENT AFFECTED NO. TITLE DTG-2754	4. JOURNAL ISSUE
5. AUTHORITY FOR CHANGE <input type="checkbox"/> INPUT <input type="checkbox"/> DOE <input type="checkbox"/> DDC <input type="checkbox"/> NASA <input type="checkbox"/> ORAL <input type="checkbox"/> WRITTEN <input type="checkbox"/> OTHER			6. ISSUED BY F. I. I.
NAME:			

7. CHANGES A. <input type="checkbox"/> DUPLICATE OF: 12-1063 670 B. <input type="checkbox"/> SUPERSEDED BY: C. <input type="checkbox"/> WITHDRAWN FROM NTIS <input type="checkbox"/> DESTROY DOCUMENT <input type="checkbox"/> RETURN DOCUMENT, MICROFORM & RELATED PAPERS TO: <input type="checkbox"/> DDC-T <input type="checkbox"/> D. <input type="checkbox"/> DISTR/AVAIL CODE:  E. <input type="checkbox"/> FILL FROM PC <input type="checkbox"/> MN <input type="checkbox"/>  F. <input type="checkbox"/> PUBLIC RELEASABILITY <input type="checkbox"/> G. <input type="checkbox"/> OTHER <input type="checkbox"/>	8. ACTION				
		DAY	HOUR	INITIAL	REMARKS
	1. REPRODUCTION	9-25		af	
	2. MICROFICHE DISTRIBUTION	9-24		me	
	3. WAREHOUSE				
	4. INVENTORY				
1) ONLY WHEN STOCK IS TRANSFERRED					

9. <input type="checkbox"/> ADP TAKE ACTION ON 1B TRANSACTION SHEET <input type="checkbox"/> ADP TAKE NO ACTION <input type="checkbox"/> ADP SCHEDULING: TAPE SALES
---

10. REMARKS
-------------

CHANGE IN DOCUMENT STATUS

NTIS-62 (REV. 1-79)  
USCOMM-DC 49769-P79

U.S. DEPARTMENT OF COMMERCE  
NATIONAL TECHNICAL INFORMATION SERVICE

2 ARCHIVES